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Rate Phenomena in the Neutral Sulfite Delignification of Loblolly Pine (*Pinus taeda* L.)

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RATE PHENOMENA IN THE NEUTRAL SULFITE DELIGNIFICATION OF LOBLOLLY PINE (*Pinus taeda* L.)

A thesis submitted by

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INTRODUCTION

There can be no doubt that the chemical delignification of wood is one of the most important steps in the manufacture of pulp and paper products. Delignification is that process whereby lignin is degraded and dissolved resulting in the liberation of cellulosic fibers from the structure of wood.

Chemical delignification processes are complicated by two factors. These are the heterogeneous nature of wood and the complex chemical and physical structure of lignin. Therefore, in order to study the reactions involved in the various delignification processes, a knowledge of the physicochemical phenomena which take place is highly important.

In this work, emphasis will be placed on the physicochemical factors which influence the kinetics of neutral sulfite delignification of wood.

HISTORICAL REVIEW

THE CHEMICAL NATURE OF SULFITE DELIGNIFICATION

According to Hägglund (1) the dissolution of lignin from wood in the sulfite process takes place as a two-stage reaction. In the first stage, solid lignin is sulfonated to form lignosulfonic acid. The second stage of the reaction involves a hydrolysis of the lignosulfonic acid to the soluble form. Erdtman (2), in a review of sulfite delignification, reports that more recent work has pointed to the existence of two types of groups in lignin which are capable of sulfonation. These reactive groups are designated as the A and B groups. The A group of lignin is capable of being sulfonated at any level of pH but if certain reactive phenols (i.e., pinosylvin, resorcinol) are present, the A group will be preferentially phenolated. The B group can be sulfonated only at low pH. Jahn (3) reports that Mikawa and co-workers have divided the A group into two groups which are called

the X and Z groups. The X groups can be sulfonated at a very rapid rate while the Z groups have a lower rate of sulfonation.

THE KINETICS OF SULFITE DELIGNIFICATION

Reaction Order

One of the earliest studies of the kinetics of the sulfite process was carried out by Stangeland (4). He showed that the "incrustants" of wood were dissolved according to a first-order reaction. Later, Corey and Maass (5) and Calhoun, Yorston, and Maass (6) conducted a series of kinetic studies in which the concentration of cooking liquor was held very nearly constant throughout the digestion. They demonstrated that the dissolution of lignin showed significant deviation from a first-order reaction. It should be noted at this point, that the use of the designation, first-order reaction, implies that the reaction is first order with respect to lignin only. Maass and co-workers (5, 6) have shown that the rate of pulping is a function of liquor concentration as well as the lignin content.

The work of Maass and co-workers was later analyzed by Goldfinger (7, 8) who attempted to determine the order of the pulping reaction. He showed that the order of the reaction is the slope of the curve obtained by plotting the logarithm of delignification rate vs. the logarithm of residual lignin. Goldfinger obtained a curve for this relationship and indicated that there is a change in the order of the pulping reaction during the cook. He attributed this change in reaction order to chemical heterogeneity of the lignin.

Activation Energy

Several investigators have measured the activation energy of the sulfite process. Corey and Maass (5) have calculated an activation energy of 21,000

cal./g.-mole compared to a value of 20,200 found by Calhoun, Yorston, and Maass (6). Goldfinger (7), on the other hand, claims that the activation energy increases from a value of 16,000 cal./g.-mole at the beginning of a cook to a value of 22,000 at the end of the cook.

Brickman, Cabott, and Purves (9) attempted to measure the activation energy of sulfonation. They reported an activation energy of sulfonation which varied from -3100 cal./g.-mole at the start of the sulfonation to 37,200 cal./g.-mole toward the end of the reaction. They stated in their paper, however, that their data may be unreliable, particularly in the early stage of the sulfonation.

Effect of Sulfonation on Reaction Rate

English, Green, Mitchell, and Yorston (10) attempted to explain the deviation of the pulping reaction from first order by assuming that the rate of sulfonation had a significant influence on the rate of the over-all reaction. They assumed that the rate of sulfonation was only a few times as fast as the rate of hydrolysis. By deriving rate equations based on this assumption, they were able to show that the shape of the delignification curve could be explained on this basis but, unfortunately, calculations based on these equations showed no agreement with experimental data. A later study of sulfonation was made by Haggroth, Lindgren, and Saeden (11) who compared delignification rates with sulfonation rates. They claim that for cooks in which the liquor has a high total sulfur dioxide content, only hydrolysis governs the delignification rate. At low total sulfur dioxide contents, the rate of sulfonation becomes an important factor in the delignification rate, particularly when the pH is less than two.

STRUCTURE OF WOOD

Harlow (12) shows Kerr and Bailey's diagram of a typical woody cell as it appears in wood. This diagram is shown in Fig. 1. Wood can be thought of as a porous material consisting of cellulosic fibers surrounded by a lignin rich material called the middle lamella. The fiber has three distinct parts, the primary wall, the secondary wall, and the lumen. The secondary wall of the fiber can be broken down further into three layers known as the S_1, S_2, and S_3 layers. The major portion of the lignin in wood is found in the middle lamella. It is known, however, that lignin is also present in the primary and secondary walls of the fiber. Bailey (13, 14), using a micromanipulator, isolated a portion of the middle lamella of Douglas-fir and found that it had a lignin content of 71% and a pentosan content of 14%.

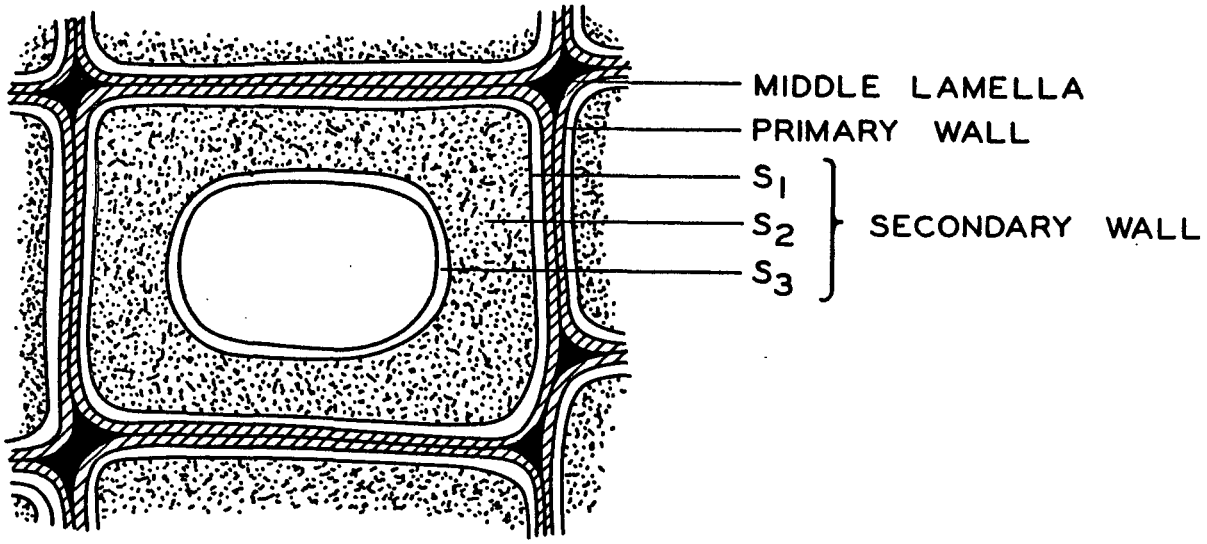

Figure 1. Cross Section of a Wood Fiber According to Harlow (12)

EFFECT OF DIGESTION ON WOOD STRUCTURE

The effect of digestion on the structure of wood was investigated by Bixler (15). He carried out the digestion of microtome cross sections of wood at several

different reaction times and observed the results under a microscope. Bixler found that soda and kraft liquors act rapidly on the middle lamella of softwood (spruce and pine) and remove the secondary wall lignin much more slowly. Sulfite liquor, on the other hand, removes the secondary wall lignin much more rapidly than soda or kraft liquors. In his investigation of the delignification of poplar, Bixler noted that the secondary wall was not visibly attacked in either of the three liquors. In all cases (softwood and hardwood) Bixler found no visible attack of the primary wall lignin. In addition, Bixler reported that the last portion of the middle lamella to be removed were the "resistant chunks" of middle lamella in the corners where three or more cells came together. In a similar study, Bucher and Widerkehr-Scherb (16) pulped sprucewood in a technical sulfite liquor and made the same observations as Bixler.

Lewis and Richardson (17) observed the swelling behavior in cuprammonium hydroxide of five pulps prepared with lignin contents ranging from 8 to 22%. In the pulps of high lignin content, only slight swelling and no ballooning was observed. As the lignin content of the pulp decreased, more swelling was observed and some ballooning began to take place. In the pulp with the lowest lignin content, there was considerable ballooning and some of the fibers dissolved. These investigators attributed this effect to a "lignin sheath" surrounding the fibers which served to protect the fibers from the action of cuprammonium hydroxide. As delignification occurred, this sheath of lignin became weaker and was partially removed.

Jayme and Köppen (18) investigated the lignin residue from sulfite and kraft pulps after hydrolysis of the carbohydrates with a mixture of concentrated hydrochloric acid and concentrated sulfuric acid (Halse lignin). In the residue from the sulfite pulps they found a small amount of finely divided, amorphous material

and in addition, some of the residue still showed a distinct fiber structure. They attributed these "lignin frames" to the external cell wall. The residue from the kraft pulps did not show any fiberlike structures but was entirely an amorphous powder. They believe that the powder which they obtained originated in the secondary wall of the fiber.

Based on the work of Lange (19) and also on their own observations, Jayme and Köppen prepared the diagram shown in Fig. 2 to demonstrate the distribution of lignin in the fiber before and after pulping. Their observations are partly confirmed by Kallmes (20) who determined the lignin concentrations across the wall of unbleached spruce sulfite fibers. Kallmes found that the P-S_1 layer contains 5.8% lignin and that the S_2 layer contains only 0.4% lignin.

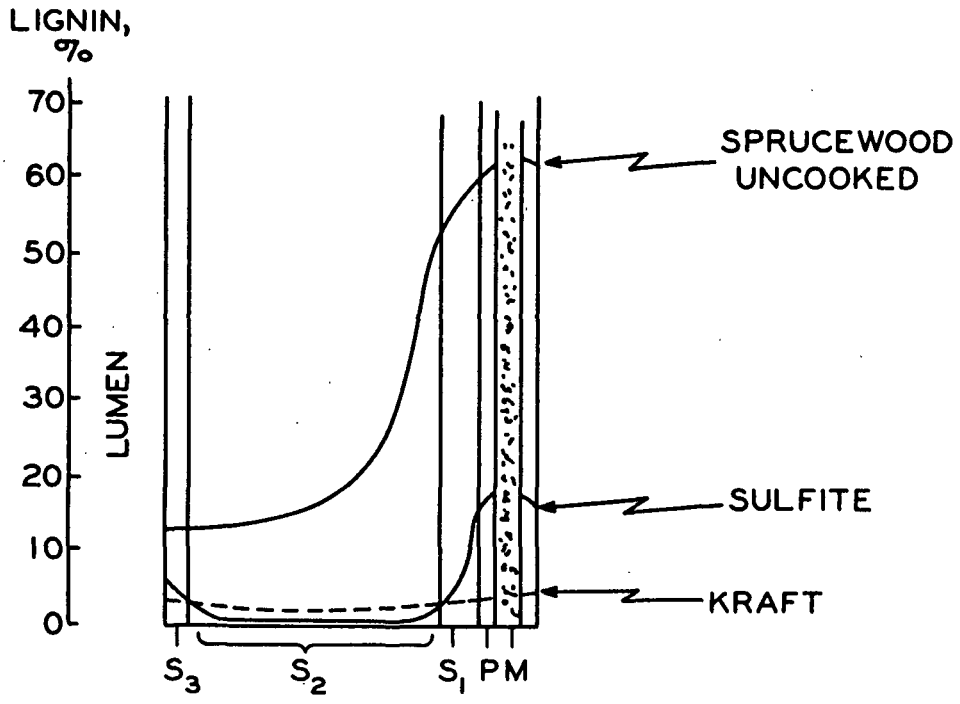

Figure 2. Distribution of Lignin in the Cell
[From Jayme and Köppen (18)]

PHYSICOCHEMICAL STUDIES

Corey and Maass (21) have advanced a hypothesis of delignification in connection with their work on the pretreatment of wood in water. They found that pretreatment of wood in water at 130°C. decreased the rate of subsequent sulfite pulping and caused even greater deviations from an assumed first-order reaction than were obtained from wood which had not been pretreated. Their explanation was that the lignin in wood exists as submicroscopic particles which agglomerate and increase in particle size when heated in aqueous solutions. They state that the increase in size caused by agglomeration of these particles is counterbalanced by the decrease in size caused by digestion in such a way that the net effect is a reaction which is approximately first order.

Nolan (22) has recently advanced another hypothesis to explain the kinetics of sulfite pulping. He claims that penetration of the wood chip does not occur but that pulping proceeds by means of a "moving reaction interface." Nolan states that delignification begins at the outside surface of a wood chip and that the reaction interface moves slowly inward towards the center of the chip.

Nokihara, Tuttle, Felicetta, and McCarthy (23) studied the molecular weight of lignin sulfonates which were isolated from the spent liquor of acid sulfite cooks on spruce and hemlock wood meal. They found the molecular weight, which was measured by diffusion, to increase with reaction time, reach a maximum, decrease to a minimum and finally rise again. These workers postulated that the smaller molecules of lignosulfonate diffused through the wood residue more rapidly than the larger molecules. The subsequent decrease and increase in the molecular weight was explained as being the result of the relative rates of hydrolysis and polycondensation of the dissolved lignin.

Goring and Rezanowich (24) found a similar relationship between the intrinsic viscosity of dissolved lignosulfonates and time. This work, however, was carried out by means of fractional delignification of spruce periodate lignin in a series of short bisulfite cooks. They also found that the sulfur content of the dissolved lignosulfonates increased as cooking time was extended. On the basis of this information, Goring and Rezanowich consider sulfite delignification to take place as a sulfonation and hydrolysis of a lignin network. Both reactions are believed to occur simultaneously. The hypothesis is made that the limiting molecular weight of soluble lignosulfonates is related to the degree of sulfonation and, as the degree of sulfonation of the insoluble lignin increases, the larger fragments which were produced by the hydrolysis become soluble. The decrease in the intrinsic viscosity after extensive cooking is considered by these workers to be caused by lignin which is highly cross linked.

PRESENTATION OF THE PROBLEM

In the past, kinetic studies of delignification have been carried out under the assumption that the reactions of lignin during cooking were of a homogeneous rather than a heterogeneous nature. Little work is recorded in which the physical and physicochemical phenomena related to the delignification process have been treated in terms of their relationship to the kinetics of the over-all process.

The purpose of this thesis is to study the neutral sulfite delignification process in terms of the morphological and physical factors which influence the rate of reaction. In order to evaluate the effects of diffusion and accessibility without seriously altering the chemical nature of the lignin, springwood and summerwood must be studied separately.

The study has been limited to loblolly pine (Pinus taeda L.) because its rapid growth ordinarily permits relatively easy separation of springwood and summerwood. This wood normally has the added advantage that the cell structures of springwood and summerwood are uniform.

EXPERIMENTAL PROCEDURES

EXPERIMENTAL PROGRAM

The experimental program consisted of a study of lignin removal and sulfur content as a function of cooking time for both low- and high-yield pulping. Changes in the concentration of cooking liquor were minimized by using a high chemical-to-wood ratio and a sodium sulfite concentration of 105 g./liter. The wood was impregnated with liquor before cooking to assure proper penetration of the sample.

The wood was separated into springwood and summerwood slivers so that the effects caused by the morphological characteristics of the wood could be studied. In order to evaluate these effects, an extensive collection of data was made at 175°C. In addition, extensive data were taken in the high-yield range at a temperature of 138.5°C. The high-yield data included a study of the effects caused by buffering of the cooking liquor and pre-extraction of the wood with acidified dioxane.

The effect of temperature on the reaction was studied by means of two additional sets of data at 184.5°C. and 196°C. The delignification at these temperatures was not studied as extensively as at 175°C.

APPARATUS

In order to obtain adequate information in the high- and low-yield range of a process which is as complex as neutral sulfite delignification, it is necessary that a large number of cooks be made. In addition, as in any kinetic study at elevated temperatures, temperature control and the time required to reach

temperature equilibrium are of prime importance. The equipment, therefore was designed to meet these requirements.

DIGESTERS

Pulping was carried out in Type 316 stainless steel autoclaves which were heated by immersion into an oil bath and cooled by quenching in ice water. Each digester was 12 inches long, had an outside diameter of 0.25 inch, and a wall thickness of 0.035 inch. Both ends of each tube were fitted with standard tube to male pipe thread connectors. The digesters were sealed by means of pipe caps. Teflon tape was used to prevent leakage. Twenty-four digesters of this type were used each of which had a volume of about 7 ml. Similar autoclaves have been described by Doraiswamy (25).

The digesters have two important advantages. A large number of cooks can be carried out within a short time and, because of their small volume and high length-to-diameter ratio, rapid heating and cooling can be achieved.

Rate of Heating and Cooling of Digesters

An experiment was performed to measure the rates of heating and cooling of the digesters when filled with water.

Temperature was measured by inserting a small thermocouple probe into the center of a digester and measuring the thermocouple output by means of a Sargent recording potentiometer. The autoclave was immersed in the hot oil bath which was set at 172°C. until temperature equilibrium was reached. Cooling was accomplished by quenching the autoclaves in ice water.

Because of lag in the recorder and in the thermocouple, the measured value of temperature is less than the actual temperature of the water in the autoclave. In order to correct for this inaccuracy, the thermocouple alone was plunged into the oil bath and its rate of response was measured.

Figure 3 shows the temperature-time relationships for the heating and cooling of the digester and the heating of the thermocouple alone. The curves which are shown represent an average of several runs. There was sufficient variation between individual runs that the results cannot be analyzed rigorously. However, temperature equilibrium was reached within 90 seconds after the digester was plunged into hot oil.

The time constants for the system were estimated from the data. A value of 1.5 seconds was obtained for the thermocouple and 14 seconds was obtained for the heating of the digester.

OIL BATH

A diagram of the oil bath is shown in Fig. 4. The bath consisted of a cylindrical tank one foot in diameter and two feet high. The walls of the tank were covered with one inch of insulation. Three electrical circuits were used to supply heat to the bath. The first circuit consisted of twelve 350-watt strip heaters located around the bottom of the tank just under the insulation. These heaters were used only for the purpose of raising the temperature of the bath very rapidly and were not used after the operating temperature had been reached. Included in this circuit was an immersion thermostat, the purpose of which was to cut off the power if the temperature of the bath exceeded 185°C. The second circuit was a coarse control circuit which was used to supply almost enough heat to

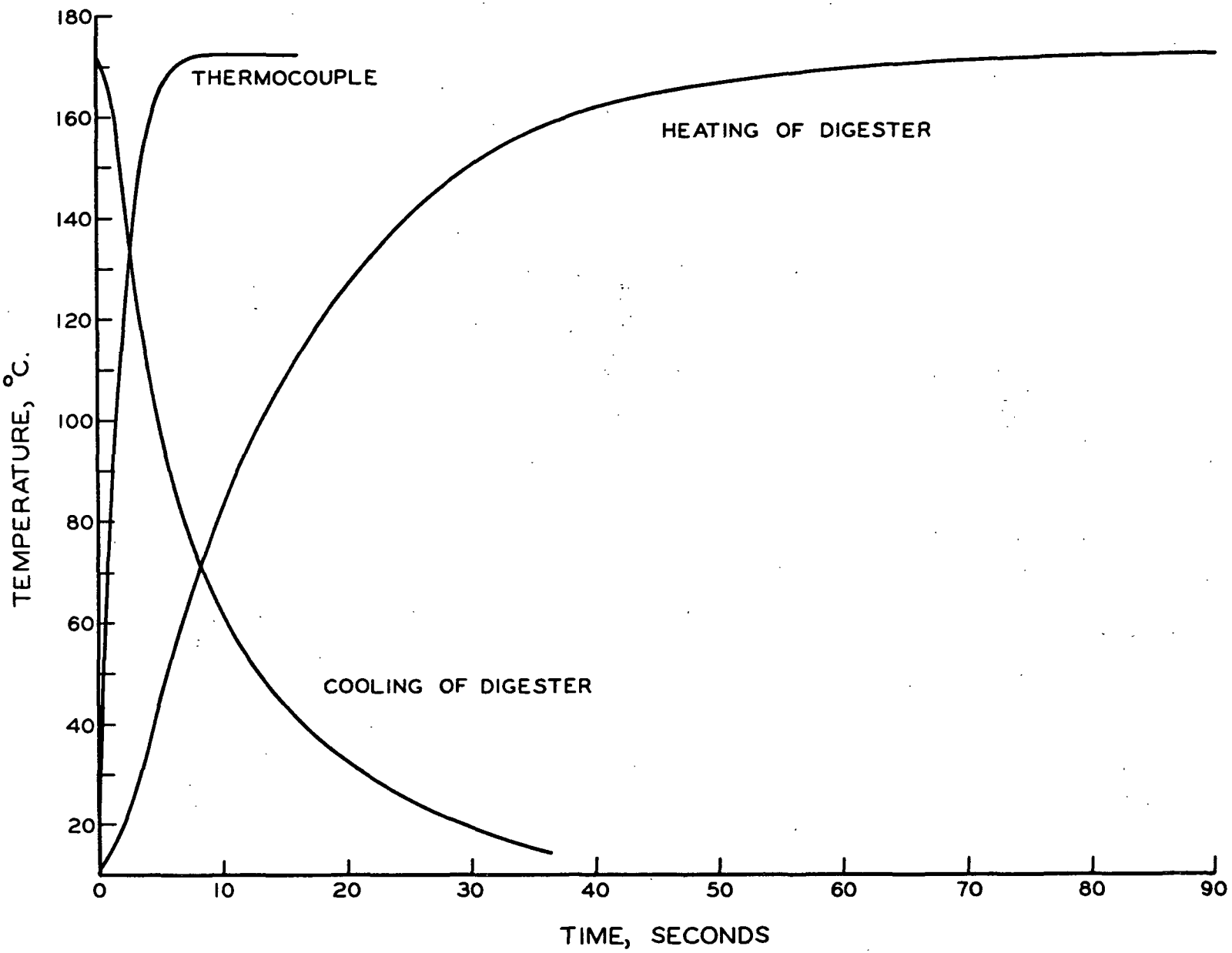

Figure 3. Heating and Cooling of Experimental Digesters

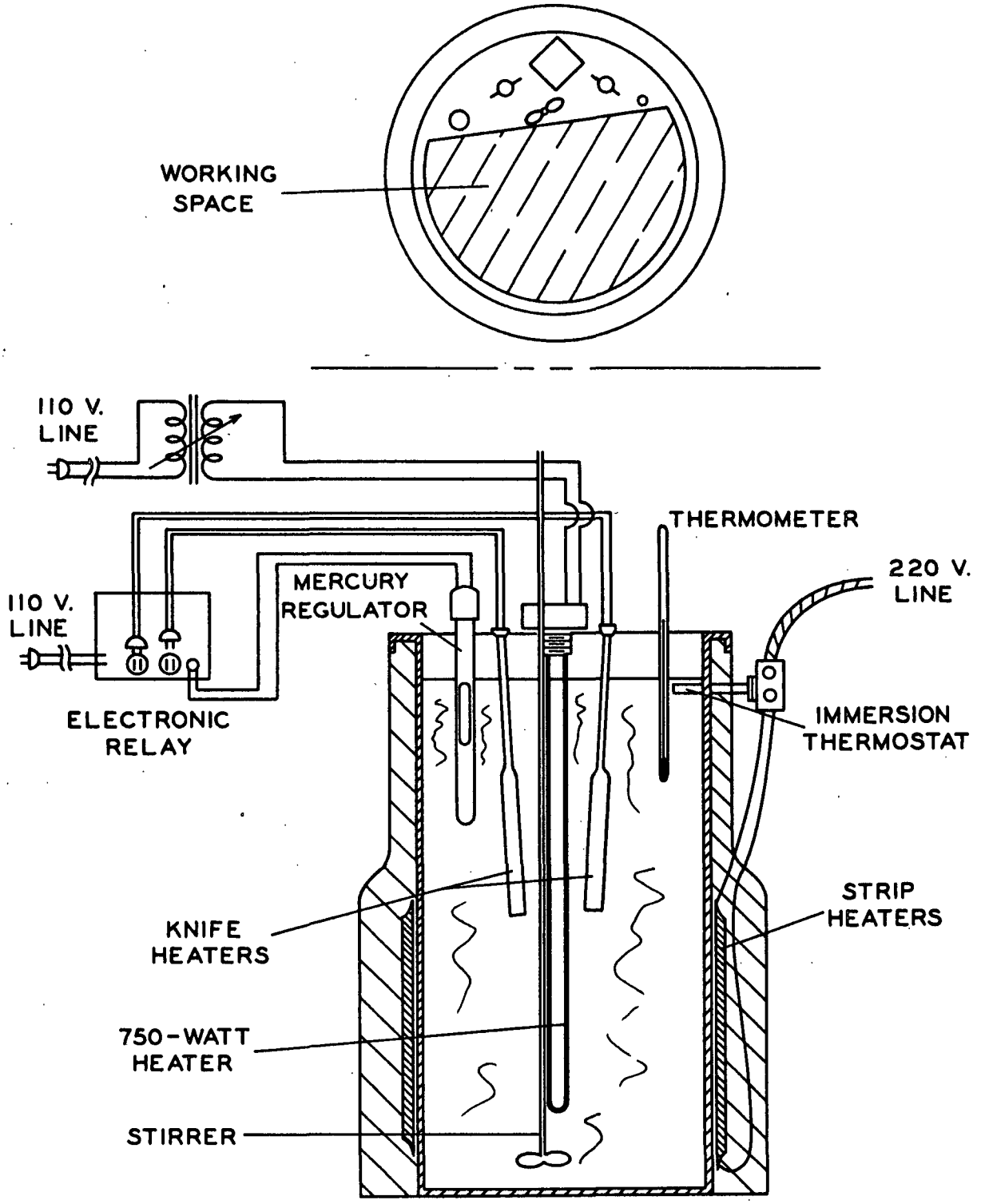

Figure 4. Diagram of Oil Bath

make up for the heat losses from the bath. This circuit consisted of a 750-watt immersion heater operated through a Powerstat variable transformer. The third circuit was a fine control circuit comprised of two 125-watt knife heaters operated through an electronic relay. The temperature sensing element was a Precision mercury regulator. The bath was agitated by means of a four-inch diameter propeller mounted on a 2-1/2 foot shaft driven by a Waco induction motor. A hood was placed over the bath to remove oil fumes.

A test was made to determine the temperature variation from point to point within the oil bath. The bath was held at 190°C. and a thermocouple was used as a temperature probe. The temperature was found to be constant within ± 0.2°C. throughout the bath except at the bath walls and near the heating elements. In addition, the temperature control of the bath was ± 0.2°C.

PROCEDURES

WOOD PREPARATION

Four sticks of loblolly pine (Pinus taeda L.) were received from the Owens-Illinois Co. The wood was cut from four trees growing in Putnam County, Georgia. After felling each tree, a cut of 63 inches was removed followed by a second cut of 48 inches which was shipped to the Institute. The diameter of each stick was 12 inches outside the bark at the large end and the wood showed fast, uniform growth.

The wood was peeled and all traces of bark and cambium were removed. In addition, 5 inches of wood was cut off the ends of each log and discarded. The logs were then cut into two-inch thick disks and those disks which were found to be free of knots or imperfections were further divided into blocks of sapwood.

Tangential slivers of summerwood and springwood were prepared by shaving the blocks on a microtome. It was found that the summerwood was more difficult to cut than the springwood and, consequently, the summerwood was cut only one-half the thickness of the springwood. The springwood slivers were sliced 0.96 mm. thick. This corresponds to about 20 fibers in thickness. On the other hand, the summerwood was cut 0.48 mm. or about 16 fibers thick.

The slivers were air dried after the shaving procedure and later cut in the longitudinal direction for the final subdivision of the wood. The final dimensions of the slivers are given in Table I.

TABLE I

DIMENSIONS OF WOOD SLIVERS

	Longitudinal Dimension, mm.	Tangential Dimension, mm.	Radial Dimension, mm.
Springwood	50	3	1.0
Summerwood	50	3	0.5

LIQUOR PREPARATION

Cooking liquor was prepared by dissolving reagent-grade sodium sulfite in distilled water which had been previously boiled to remove dissolved air and stored under nitrogen. The concentration of the liquor was determined by measurement of its total sulfur dioxide content. Institute Method 110 was used for this purpose. The liquor was acidified with a small amount of dilute hydrochloric acid before analysis.

Fresh liquor having a sodium sulfite concentration of 105 g./liter was prepared for each series of cooks.

Potentiometric Titration of Cooking Liquor

Figure 5 shows the result of the potentiometric titration of a 105 g./liter solution of sodium sulfite with 17.35N acetic acid. The choice of acetic acid was made because it approximates the natural acids found in wood. The data for this experiment are presented in Table II.

TABLE II

POTENTIOMETRIC TITRATION OF COOKING LIQUOR

Sodium Sulfite = 1000 ml. at 105 g./liter

Acetic Acid = 17.35N

Acetic Acid, ml.	pH	Neutralization,[a] %	Acetic Acid, ml.	pH	Neutralization, %
0	9.90	0	5.0	7.48	5.23
0.3	8.79	0.31	7.5	7.29	7.84
0.6	8.47	0.63	10.0	7.10	10.45
1.0	8.22	1.05	15.0	6.87	15.66
1.5	8.05	1.57	20.0	6.65	20.90
2.0	7.91	2.09	25.0	6.50	26.15
2.5	7.81	2.62	30.0	6.30	31.35
3.5	7.65	3.66	40.0	5.97	41.80

[a]Based on sodium sulfite concentration.

PULPING PROCEDURE

Cooking the Wood

Thirteen springwood slivers (0.6 g.) or 12 summerwood slivers (0.8 g.) of known ovendry content were used for each cook. After each sample of slivers was weighed on an analytical balance, it was placed in a test tube and covered with

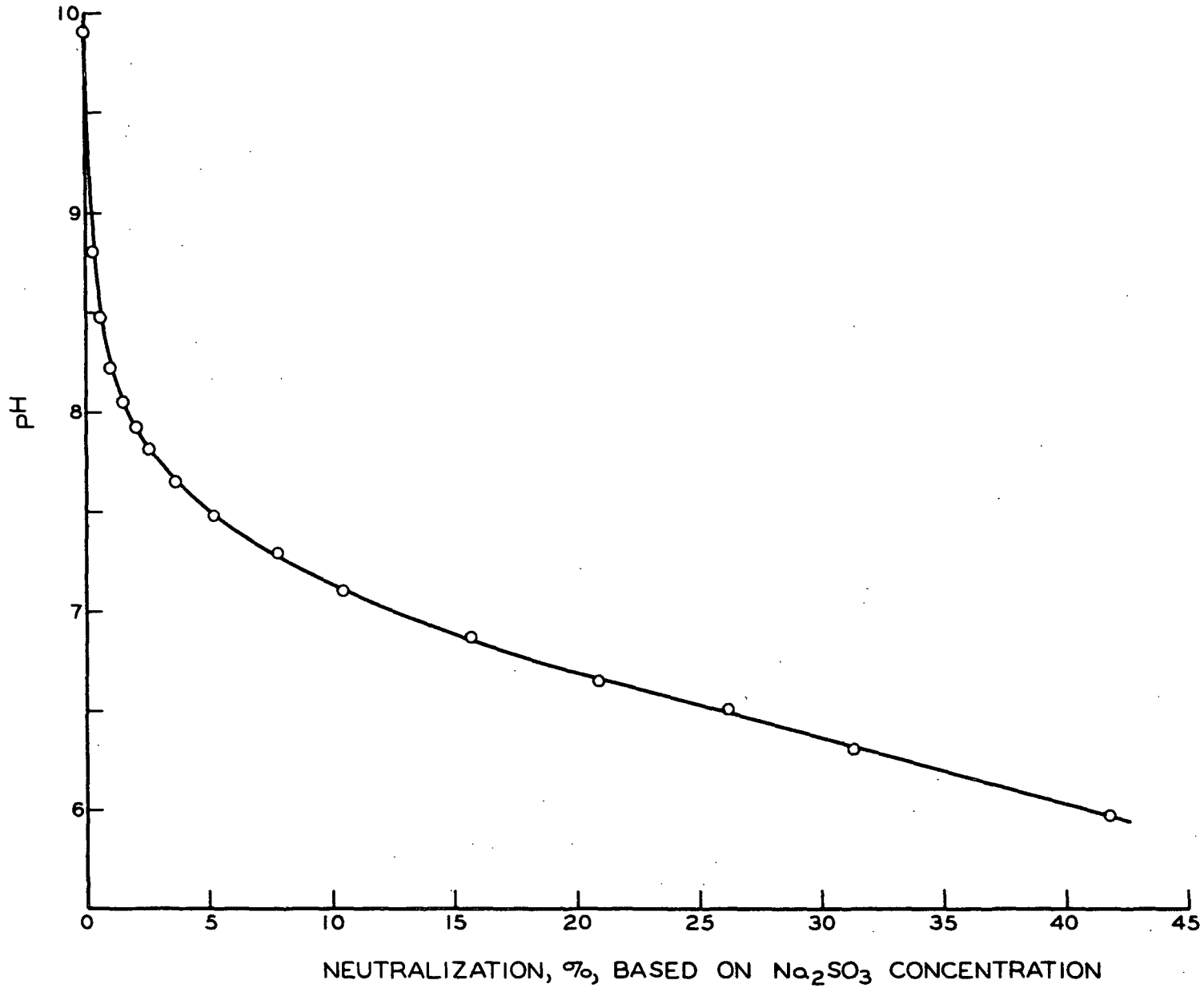

Figure 5. Potentiometric Titration of Cooking Liquor

cooking liquor. The slivers were kept from floating in the liquor by means of a small piece of wire gauze which fit snugly into the test tube and was placed over the slivers. The sample was then placed under vacuum for 30 minutes to deaerate the wood. Occasional shaking of the test tube was necessary to release air bubbles clinging to the wood and wire gauze. After the vacuum was released, the slivers were allowed to soak for ten minutes while penetration took place. While the slivers were soaking, the required volume of cooking liquor was placed in a digester by means of a hypodermic syringe. Finally, the slivers were removed from the test tube and placed, two at a time, into the digester. Nitrogen was introduced into the air space above the liquor and the digester was sealed. Cooking time was measured from the time the digester was placed into the oil bath until the time that the digester was quenched in ice water.

The volume of cooking liquor which was placed in the digester was approximately 4.8 ml. for the summerwood and 3.8 ml. for the springwood. The liquor uptake of the wood during the penetration step was approximately 0.3 ml. for the summerwood and 1.5 ml. for the springwood. The approximate ratio of liquor volume to wood weight therefore, was 6.4 ml./g. for summerwood and 8.8 ml./g. for springwood.

Washing the Pulp

After cooking, the contents of each digester were disintegrated in a Waring Blendor and washed with about 1000 ml. of distilled water on a tared, coarse sintered-glass filter. The pulp was then soaked in the cold room overnight at 40°F. in 50 ml. of distilled water and filtered the following day. Fresh distilled water was added and the pulp was again soaked overnight in the cold room. The process of overnight soaking and filtering was repeated three times for pulps which were

to be used in the lignin analysis and six times for the pulps which were to be used for sulfur analysis. The data of Marth (26) indicate that three soakings are more than is necessary to remove all but small traces of cooking liquor from the pulp.

Yields were determined without sample transfer by weighing the sample and filter together. For the pulps which were to be used for the lignin analysis, washing was carried out on tared, coarse sintered-glass extraction thimbles so that the pulp could be extracted without the need of sample transfer.

CHEMICAL ANALYSIS

Two cooks were made at each condition of time and temperature. One cook was used for the lignin determination and the other was used to measure the yield and sulfur content.

Lignin was measured as the sum of the Klason lignin and soluble lignin. The analysis was started after three sequences of soaking the pulp.

Sulfur content was determined by combustion of the pulp in the Leco furnace. In this technique the gaseous products of combustion are analyzed for sulfur dioxide by means of an iodometric titration. Sulfur analysis was carried out after six washing sequences.

The lignin and sulfur determinations are discussed more thoroughly in APPENDIX I.

EXPERIMENTAL DATA

The experimental pulping data are presented in Tables III and IV. Table III shows the results of the lignin analysis of uncooked wood. Table IV contains the yield, sulfur analysis, and lignin analysis of all cooks which were made in this investigation.

Each cook is identified by four symbols. The first symbol is the cooking temperature in degrees centigrade, the second identifies the sample as springwood (Sp) or summerwood (Sm), the third is an identification number, and the fourth symbol identifies the cooking conditions. In the fourth symbol, the letter (B) refers to the use of buffered cooking liquor, (U) refers to unbuffered liquor, and (D) refers to wood which was previously extracted with acidified dioxane.

The following is an example of the use of this numbering system. In Cook Number 138.5-Sp-7-BD, the cooking temperature was 138.5°C., the wood was a sample of springwood, the cook was Number 7 of the series, and the sample was pre-extracted with acidified dioxane and cooked in a buffered liquor. In the lignin analysis of the uncooked wood, the first symbol was omitted and the symbol (N) refers to untreated wood.

The residual lignin content and sulfur content of each pulp was calculated as a percentage of the original lignin content of the wood. This was done to allow direct comparison of the data for springwood and summerwood and to keep the values of these quantities on a stable basis. The following relationships were used to convert the raw data to this basis.

$$\%, \text{ Wood Basis} = (\%, \text{ Pulp Basis})(\text{Yield}, \%)/100$$

$$\%, \text{ Lignin Basis} = 100\ (\%, \text{ Wood Basis})/(\text{Original Wood Lignin}, \%)$$

TABLE III

LIGNIN ANALYSIS OF UNCOOKED WOOD

Sample Number	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Yield of Extr. Wood, %
Sp-01-D	25.3	0.4	25.7	86.9
Sp-02-D	25.1	0.6	25.7	86.9
Sp-01-N	28.2	0.3	28.5	
Sp-02-N	28.2	0.3	28.5	
Sp-03-N	28.3	0.3	28.6	
Sm-04-N	25.7	0.3	26.0	
Sm-05-N	25.6	0.3	25.9	
Sm-06-N	25.6	0.3	25.9	

TABLE IV

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
138.5-Sp-2-B	30.000 m.	7.59	93.3	26.5	0.8	27.3	0.585	95.7	2.05
138.5-Sp-1-B	45.000 m.	7.59	92.2	25.8	1.0	26.8	0.638	93.9	2.24
138.5-Sp-3-B	45.000 m.	7.56	92.3	26.0	0.9	26.9	0.706	94.3	2.48
138.5-Sp-4-B	1.000 h.	7.60	92.2	25.7	1.1	26.8	0.650	93.8	2.28
138.5-Sp-5-B	1.500 h.	7.55	92.0	25.3	1.4	26.7	0.737	93.8	2.59
138.5-Sp-6-B	2.000 h.	7.54	91.2	25.4	1.5	26.9	0.721	94.3	2.53
138.5-Sp-7-B	2.500 h.	7.53	91.0	24.7	1.6	26.3	0.734	92.2	2.57
138.5-Sp-8-B	4.000 h.	7.60	90.0	24.3	1.9	26.2	0.766	91.9	2.69
138.5-Sp-9-B	6.500 h.	7.57	88.9	24.2	2.0	26.2	0.815	91.8	2.86
138.5-Sp-10-B	6.500 h.	7.57	88.5	23.7	2.0	25.7	0.842	90.2	2.95
138.5-Sp-11-B	9.000 h.	7.53	88.0	23.3	2.3	25.6	0.821	89.9	3.06
138.5-Sp-12-B	12.000 h.	7.52	87.6	22.6	2.6	25.2	0.830	88.3	2.91
138.5-Sm-13-B	30.000 m.	7.51	95.4	23.6	0.7	24.3	0.603	94.0	2.33
138.5-Sm-14-B	33.000 m.	7.49	95.2	23.6	0.7	24.3	0.617	93.8	2.38
138.5-Sm-15-B	45.000 m.	7.53	94.6	22.8	0.9	23.7	0.683	91.4	2.64
138.5-Sm-16-B	1.000 h.	7.51	94.4	22.5	1.1	23.6	0.695	91.3	2.68
138.5-Sm-17-B	1.500 h.	7.53	93.7	21.7	1.6	23.3	0.726	90.0	2.81
138.5-Sm-18-B	2.000 h.	7.53	92.7	21.5	1.7	23.2	0.717	89.4	2.77
138.5-Sm-19-B	2.500 h.	7.56	92.5	21.1	1.6	22.7	0.787	87.6	3.04
138.5-Sm-20-B	2.500 h.	7.56	93.0	21.4	1.8	23.2	0.769	89.7	2.97
138.5-Sm-21-B	4.000 h.	7.54	92.2	20.9	2.0	22.9	0.800	88.4	3.09
138.5-Sm-22-B	6.500 h.	7.56	90.7	19.5	2.5	22.0	0.795	84.9	3.07
138.5-Sm-23-B	9.000 h.	7.54	89.3	19.7	2.4	22.1	0.820	85.3	3.17
138.5-Sm-24-B	12.000 h.	7.51	88.4	19.1	2.5	21.6	0.813	83.1	3.14

[a]Time is reported in minutes (m.) and hours(h.).

TABLE IV (Continued)

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
138.5-Sp-1-U	15.000 m.	--	92.6	26.8	0.5	27.3	0.517	95.9	1.81
138.5-Sp-2-U	15.000 m.	--	92.5	26.8	0.6	27.4	0.492	95.9	1.73
138.5-Sp-3-U	30.000 m.	--	91.8	26.3	0.8	27.1	0.551	95.0	1.93
138.5-Sp-4-U	45.000 m.	--	90.9	26.2	0.9	27.1	0.610	95.0	2.14
138.5-Sp-5-U	1.000 h.	--	90.7	25.2	1.0	26.2	0.710	91.9	2.49
138.5-Sp-6-U	1.000 h.	--	90.2	25.9	1.1	27.0	0.644	94.5	2.26
138.5-Sp-7-U	1.500 h.	--	89.9	24.9	1.3	26.2	0.692	91.8	2.43
138.5-Sp-8-U	2.000 h.	--	89.2	24.4	1.5	25.9	0.750	91.0	2.63
138.5-Sp-9-U	2.500 h.	--	88.5	24.4	1.5	25.9	0.685	90.9	2.40
138.5-Sp-10-U	3.500 h.	--	87.8	24.0	1.7	25.7	0.743	90.2	2.61
138.5-Sp-11-U	6.000 h.	--	86.8	23.2	2.1	25.3	0.767	89.7	2.69
138.5-Sp-12-U	10.000 h.	--	85.1	22.5	2.3	24.8	0.921	87.1	3.23
138.5-Sp-1A-U	2.000 h.	8.11	--	--	--	--	--	--	--
138.5-Sp-2A-U	4.000 h.	8.02	--	--	--	--	--	--	--
138.5-Sm-13-U	15.000 m.	--	95.3	24.0	0.6	24.6	0.460	94.9	1.77
138.5-Sm-14-U	30.000 m.	--	94.0	22.9	0.9	23.8	0.563	91.8	2.17
138.5-Sm-15-U	45.000 m.	--	92.7	22.3	1.1	23.4	0.687	90.6	2.65
138.5-Sm-16-U	1.500 h.	--	92.5	21.4	1.5	22.9	0.741	88.1	2.86
138.5-Sm-17-U	2.500 h.	--	--	20.6	2.4	23.0	--	88.8	--
138.5-Sm-18-U	2.500 h.	--	90.9	20.4	2.4	22.8	0.822	88.1	3.17
138.5-Sm-19-U	3.500 h.	--	90.4	20.5	2.5	23.0	0.820	88.6	3.16
138.5-Sm-20-U	5.000 h.	--	89.8	20.2	2.4	22.6	0.851	86.9	3.29
138.5-Sm-21-U	6.500 h.	--	88.7	--	--	--	0.861	--	3.33
138.5-Sm-22-U	6.500 h.	--	88.2	20.1	2.6	22.7	0.825	87.9	3.19
138.5-Sm-23-U	8.250 h.	--	88.4	20.0	2.5	22.5	0.918	86.6	3.55
138.5-Sm-24-U	10.000 h.	--	87.9	18.2	3.1	21.3	0.867	82.0	3.35

[a]Time is reported in minutes (m.) and hours (h.).

TABLE IV (Continued)

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
175-Sp-1-U	4.093 m.	--	90.1	25.2	0.8	26.0	0.573	91.3	2.01
175-Sp-2-U	7.600 m.	--	88.4	24.9	1.0	25.9	0.640	90.7	2.24
175-Sp-3-U	10.000 m.	--	87.8	23.9	1.2	25.2	0.664	88.2	2.33
175-Sp-4-U	14.000 m.	--	87.2	23.0	1.3	24.3	0.701	85.4	2.46
175-Sp-5-U	14.000 m.	--	86.9	23.0	1.3	24.3	0.678	85.1	2.38
175-Sp-6-U	20.000 m.	--	85.5	22.6	1.5	24.1	0.698	84.7	2.45
175-Sp-7-U	30.000 m.	--	83.9	21.8	1.7	23.5	0.712	82.4	2.50
175-Sp-8-U	45.000 m.	--	82.3	19.1	1.8	20.9	0.648	73.3	2.27
175-Sp-18-U	1.000 h.	--	81.3	19.2	2.6	21.8	0.662	76.6	2.32
175-Sp-10-U	1.000 h.	--	80.3	17.3	2.6	19.9	0.642	69.9	2.25
175-Sp-11-U	1.500 h.	--	77.7	17.1	3.1	20.2	0.663	71.0	2.33
175-Sp-12-U	2.000 h.	--	73.6	15.2	3.0	18.2	0.623	63.8	2.18
175-Sp-13-U	2.500 h.	--	70.2	12.1	3.1	15.2	0.546	53.2	1.91
175-Sp-14-U	3.000 h.	--	67.7	10.3	3.0	13.3	0.497	46.6	1.74
175-Sp-15-U	4.000 h.	--	63.7	7.3	2.9	10.2	0.418	35.8	1.47
175-Sp-16-U	5.000 h.	--	57.3	6.3	2.7	9.0	0.330	31.7	1.16
175-Sp-17-U	6.000 h.	--	53.2	4.0	2.1	6.1	0.242	21.4	0.85
175-Sp-9-U	7.000 h.	--	51.1	2.8	2.1	4.9	0.214	17.0	0.75
175-Sp-19-U	7.000 h.	--	49.3	3.9	2.5	6.4	0.190	22.5	0.67
175-Sp-20-U	8.083 h.	--	47.0	1.7	2.0	3.7	0.148	13.1	0.52
175-Sp-21-U	10.000 h.	--	44.9	0.9	1.6	2.5	0.132	8.7	0.46
175-Sp-22-U	12.000 h.	--	41.2	0.2	1.1	1.3	0.077	4.5	0.27
175-Sp-23-U	12.000 h.	--	42.3	0.3	1.2	1.5	0.087	5.3	0.31
175-Sp-24-U	14.000 h.	--	39.7	0.2	0.8	1.0	0.062	3.5	0.22

[a]Time is reported in minutes (m.) and hours (h.).

TABLE IV (Continued)

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
175-Sm-1-U	4.995 m.	--	92.8	22.9	1.2	24.1	0.632	92.9	2.44
175-Sm-2-U	10.033 m.	--	90.4	20.9	1.6	22.5	0.702	87.0	2.71
175-Sm-3-U	14.996 m.	--	90.2	20.6	1.8	22.4	0.731	86.7	2.82
175-Sm-5-U	20.000 m.	--	89.2	19.7	--	--	0.729	--	2.81
175-Sm-4-U	21.500 m.	--	88.6	19.1	2.0	21.1	0.735	81.2	2.83
175-Sm-6-U	30.000 m.	--	87.5	18.8	2.5	21.3	0.718	82.3	2.77
175-Sm-7-U	45.000 m.	--	84.5	17.0	2.9	19.9	0.744	76.8	2.87
175-Sm-8-U	1.000 h.	--	84.9	16.0	3.0	19.0	0.757	73.3	2.92
175-Sm-9-U	1.500 h.	--	79.9	14.1	3.3	17.4	0.655	67.1	2.53
175-Sm-10-U	2.000 h.	--	77.5	--	--	--	0.619	--	2.39
175-Sm-11-U	2.500 h.	--	73.9	10.8	3.6	14.4	0.582	55.8	2.25
175-Sm-12-U	3.000 h.	--	74.4	10.6	3.7	14.3	0.597	55.1	2.31
175-Sm-13-U	4.000 h.	--	68.5	8.6	2.6	11.2	0.440	43.1	1.70
175-Sm-14-U	4.000 h.	--	68.4	9.1	3.1	12.2	0.483	47.1	1.86
175-Sm-15-U	5.000 h.	--	63.9	7.4	2.4	9.8	0.427	38.0	1.65
175-Sm-16-U	6.017 h.	--	59.8	3.7	2.6	6.3	0.298	24.3	1.15
175-Sm-17-U	8.000 h.	--	54.9	2.3	2.3	4.6	0.217	17.7	0.84
175-Sm-18-U	8.000 h.	--	53.9	2.3	2.3	4.6	0.207	17.7	0.80
175-Sm-19-U	10.000 h.	--	49.6	0.7	1.8	2.5	0.132	9.5	0.51
175-Sm-20-U	12.000 h.	--	47.4	0.3	1.6	1.9	0.105	7.2	0.40
175-Sm-21-U	14.000 h.	--	45.2	0.2	1.2	1.4	0.084	5.5	0.33
175-Sm-22-U	14.000 h.	--	45.6	0.1	1.2	1.3	0.081	5.0	0.31
175-Sm-23-U	16.000 h.	--	43.1	0.1	0.9	1.0	0.066	3.9	0.25
175-Sm-24-U	18.000 h.	--	40.3	0.1	0.7	0.8	0.057	3.1	0.22

[a]Time is reported in minutes (m.) and hours (h.).

TABLE IV (Continued)

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
185-Sp-14-U	0.250 h.	7.99	84.9	21.3	1.5	22.8	0.680	79.9	2.39
185-Sp-15-U	1.000 h.	8.08	75.5	15.2	2.7	17.9	0.549	62.7	1.93
185-Sp-13-U	2.250 h.	8.34	59.8	7.4	2.7	10.1	0.362	35.6	1.27
185-Sp-16-U	3.750 h.	8.53	48.6	1.8	2.1	3.9	0.233	13.8	0.82
185-Sp-17-U	5.000 h.	8.58	42.5	0.1	1.7	1.8	0.098	6.4	0.34
185-Sp-18-U	6.000 h.	8.76	40.5	0.1	1.1	1.2	0.071	4.1	0.25
185-Sm-20-U	0.250 h.	7.95	86.9	17.8	2.3	20.1	0.712	77.6	2.75
185-Sm-21-U	1.000 h.	7.99	77.6	12.8	3.0	15.8	0.555	61.1	2.14
185-Sm-19-U	2.250 h.	8.34	65.6	6.7	2.5	9.2	0.398	35.5	1.54
185-Sm-22-U	3.750 h.	8.53	49.1	2.4	2.1	4.5	0.190	17.5	0.73
185-Sm-23-U	5.000 h.	8.23	47.9	0.2	1.6	1.8	0.131	7.1	0.50
185-Sm-24-U	6.000 h.	8.58	45.9	0.1	1.4	1.5	0.093	5.9	0.36
196-Sp-4-U	0.338 h.	8.05	76.2	17.0	1.8	18.8	0.529	66.1	1.85
196-Sp-2-U	0.750 h.	8.19	63.9	9.5	2.3	11.8	0.381	41.3	1.34
196-Sp-3-U	1.500 h.	8.30	48.3	1.7	1.8	3.5	0.164	12.3	0.58
196-Sp-1-U	2.250 h.	8.29	40.0	0.1	1.1	1.2	0.071	4.3	0.25
196-Sp-5-U	3.000 h.	8.47	36.3	0.0	0.6	0.6	0.051	2.3	0.18
196-Sp-6-U	3.500 h.	8.41	33.3	0.1	0.3	0.4	0.045	1.4	0.16
196-Sm-10-U	0.338 h.	7.94	80.4	14.3	2.7	17.0	0.562	65.5	2.17
196-Sm-8-U	0.750 h.	8.06	67.4	8.1	2.3	10.4	0.401	40.3	1.55
196-Sm-9-U	1.500 h.	8.18	52.4	1.7	2.2	3.9	0.174	15.1	0.67
196-Sm-7-U	2.250 h.	8.33	45.1	0.1	1.3	1.4	0.099	5.6	0.38
196-Sm-11-U	3.000 h.	8.19	40.9	0.0	0.8	0.8	0.069	2.9	0.27
196-Sm-12-U	3.500 h.	8.32	38.6	0.0	0.5	0.5	0.055	2.0	0.21

[a]Time is reported in minutes (m.) and hours (h.).

TABLE IV (Continued)

PULPING DATA

Cook Number	Cooking[a] Time	Spent Liquor pH	Yield, %	Klason Lignin, % of wood	Soluble Lignin, % of wood	Total Lignin, % of wood	Sulfur, % of wood	Total Lignin, % of original	Sulfur, % of original lignin
138.5-Sp-1-BD	0.500 h.	7.63	81.4	24.1	1.1	25.2	--	88.3	--
138.5-Sp-2-BD	0.750 h.	7.52	80.9	23.8	1.3	25.1	--	88.1	--
138.5-Sp-3-BD	1.000 h.	--	80.7	23.5	1.5	25.0	--	87.9	--
138.5-Sp-4-BD	1.000 h.	7.55	80.7	23.8	1.5	25.3	--	88.6	--
138.5-Sp-5-BD	1.500 h.	--	80.0	22.5	2.4	24.9	--	87.6	--
138.5-Sp-6-BD	2.000 h.	7.61	79.8	22.1	2.6	24.7	--	86.8	--
138.5-Sp-7-BD	2.500 h.	--	79.3	21.8	3.0	24.8	--	86.8	--
138.5-Sp-8-BD	2.500 h.	7.62	79.6	21.4	3.0	24.4	--	85.7	--
138.5-Sp-9-BD	4.000 h.	7.56	78.9	21.2	3.5	24.7	--	86.8	--
138.5-Sp-10-BD	6.500 h.	7.59	78.0	20.2	4.4	24.6	--	86.3	--
138.5-Sp-11-BD	9.000 h.	7.60	77.5	19.6	4.4	24.0	--	84.3	--
138.5-Sp-12-BD	12.000 h.	7.58	76.6	19.8	4.5	24.3	--	85.2	--

[a]Time is reported in minutes (m.) and hours (h.).

RESULTS AND DISCUSSION

The neutral sulfite delignification of wood will be considered to follow four basic steps.

1. Diffusion of cooking chemical through the wood structure to the surface of lignin particles.
2. Sulfonation of the lignin.
3. Hydrolysis of the lignin.
4. Diffusion of the reaction products away from the lignin particles out of the wood.

The second and third steps of the process are the chemical reaction steps proposed by Hägglund (1) for acid sulfite pulping. These reaction steps are considered to be affected by the physical accessibility of the lignin.

Brauns (27) cites the evidence of several workers which indicates that lignin has an amorphous structure. Such a structure, if porous, is likely to be accessible to penetration by molecules or ions of cooking chemical. If this is true, and if lignin is considered to exist as small particles in the wood, one might expect the chemical reactions of delignification to take place in a three-dimensional zone on the surface of the lignin particle. Below this three-dimensional surface a substrate of unreacted lignin can exist. As delignification proceeds, the lignin particles become smaller in size and there will be a corresponding decrease in the amount of unreacted lignin.

The existence of an unreacted lignin substrate is not easily established. Clearly, such a phenomenon will be related to the size of the lignin particle, the porosity of the lignin molecule, and the rate of diffusion of active chemical into the lignin structure. In addition, it is not necessary to expect to find a sharp

dividing line between the reaction zone and the unreacted substrate; instead, a diffuse gradient might exist.

One other phenomenon can be postulated as a result of the assumption that lignin exists as particles. Products of the delignification reaction, which are formed by the degradation of molecules located within the zone of reaction, must diffuse through the structure of insoluble lignin to the surface of the lignin particle. Because of their high molecular weight (23, 24), these reaction products can become immobilized by the lignin structure. This will result in a lowering of the apparent rate of delignification.

The effects caused by either an unreacted lignin substrate or the immobilization of reaction products would be difficult to separate in a kinetic study. For this reason, both of these phenomena have been combined in this study and are called the physical accessibility of the lignin.

The preceding analysis of delignification shows that the chemical reaction steps can have certain characteristics of both homogeneous and heterogeneous reactions.

The diffusion steps of the process can be divided into three parts; diffusion in the bulk phase of the liquor outside of the wood chip, diffusion through the porous structure of the wood, and diffusion between the large pores and the surface of the lignin particles. The porous structure which is referred to is the lumen system of the wood. Beazley, Johnston, and Maass (28) suggest that diffusion through the tracheids is the main diffusion route in neutral or acid solutions.

Diffusion between the lumen and the surface of lignin particles is the step of the diffusion process which is most seriously affected by the morphology of wood. Removal of the cell wall lignin requires diffusion through the cell wall. For removal of the middle lamella lignin, the cell wall is not necessarily the preferred path of diffusion. The studies of Lange (29) indicate that the middle lamella may actually be more porous than the secondary wall. If this is true, diffusion through pits and the porous middle lamella may be a path which has a lower diffusional resistance than the cell wall.

In the following discussion, the experimental data is examined in terms of the foregoing analysis. The assumption will be made throughout the discussion that there are no significant differences between the chemical nature of cell wall lignin and middle lamella lignin. Any differences in the delignification of the cell wall or middle lamella will be considered to be a result of physical differences between the two.

The sulfonation and hydrolysis steps of the reaction are discussed in terms of their homogeneous aspects and the heterogeneity of the reactions is discussed separately as the physical accessibility of the lignin.

DIFFUSION STEPS

Before chemical reaction can take place it is necessary for the active species of the cooking liquor to diffuse to the surface of the lignin particles. In the system which has been studied, however, this effect was minimized by preimpregnation of the wood with cooking liquor before starting the reaction. In this way it was possible to utilize the void volume of the wood to act as reservoirs of cooking liquor. It is shown in APPENDIX II that, because of its high concentration,

the amount of liquor which was introduced into the wood before cooking contained sufficient cooking chemical to complete the delignification reaction. It follows, therefore, that the preimpregnation procedure helped to maintain a high concentration of reactants at the reaction sites and hence decreased any effect that diffusion of reactants might have on the over-all rate of reaction.

If one is to consider the effect of either of the two diffusion steps on the over-all reaction rate, it would seem reasonable that the diffusion of reaction products would have the largest effect. The molecular weight of delignification reaction products has been shown by McCarthy and co-workers (23) and Goring and Rezanowich (24), to have a lower limit of about 3000. Since this molecular weight is considerably higher than the molecular weight of the active cooking chemical, one would expect the rate of reaction product diffusion to be less than the rate of diffusion of cooking chemical.

EFFECT OF PRODUCT DIFFUSION ON RATE

In the collection of experimental data, the wood was separated into springwood and summerwood chips and each was pulped separately. Microscopic examination of the wood showed the cell wall of the summerwood fibers to be approximately four times the thickness of the springwood cell walls. In addition, it is shown in APPENDIX III that if one assumes that the lignin in springwood is situated mainly in the middle lamella and primary wall, the summerwood will contain at least 50% of its lignin in the secondary walls of the fibers. Thus, the summerwood can be used to determine the effect that diffusion of reaction products through the cell wall has on the delignification rate.

In Fig. 6, 7, and 8, the residual lignin content of springwood and summerwood is plotted vs. cooking time. The curves of Fig. 6 show that after the residual

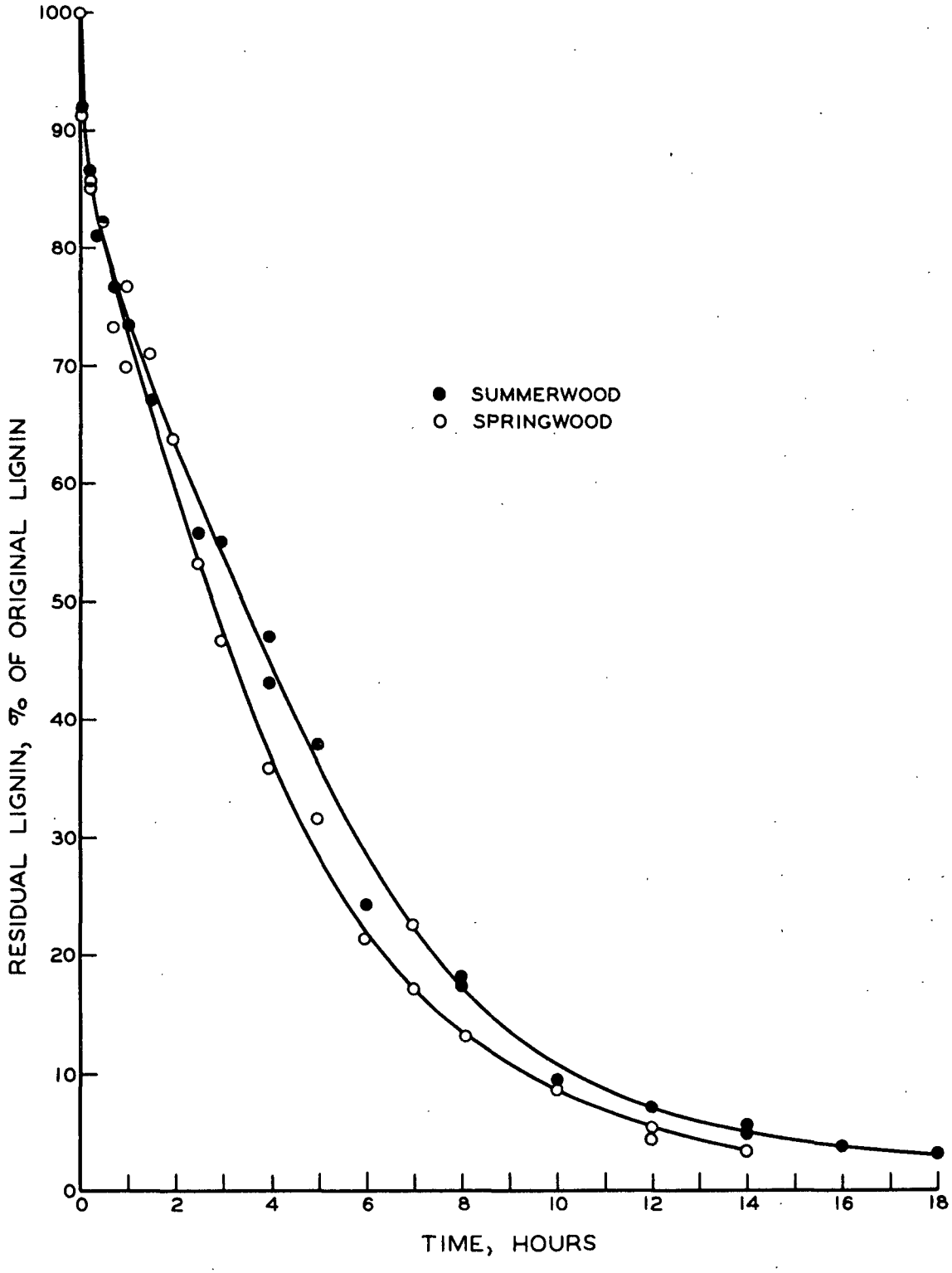

Figure 6. Delignification of Springwood and Summerwood at 175°C.

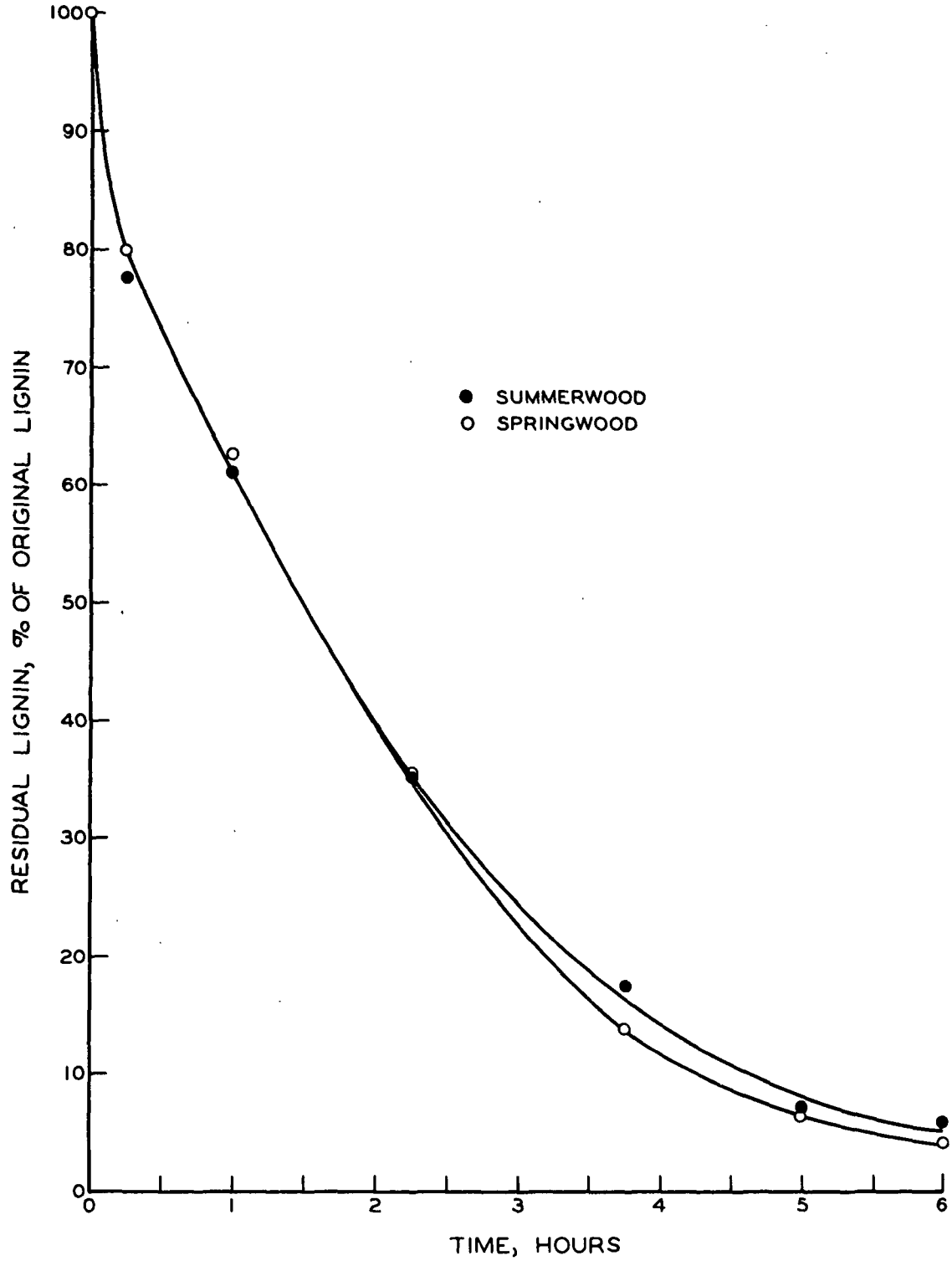

Figure 7. Delignification of Springwood and Summerwood at 184.5°C.

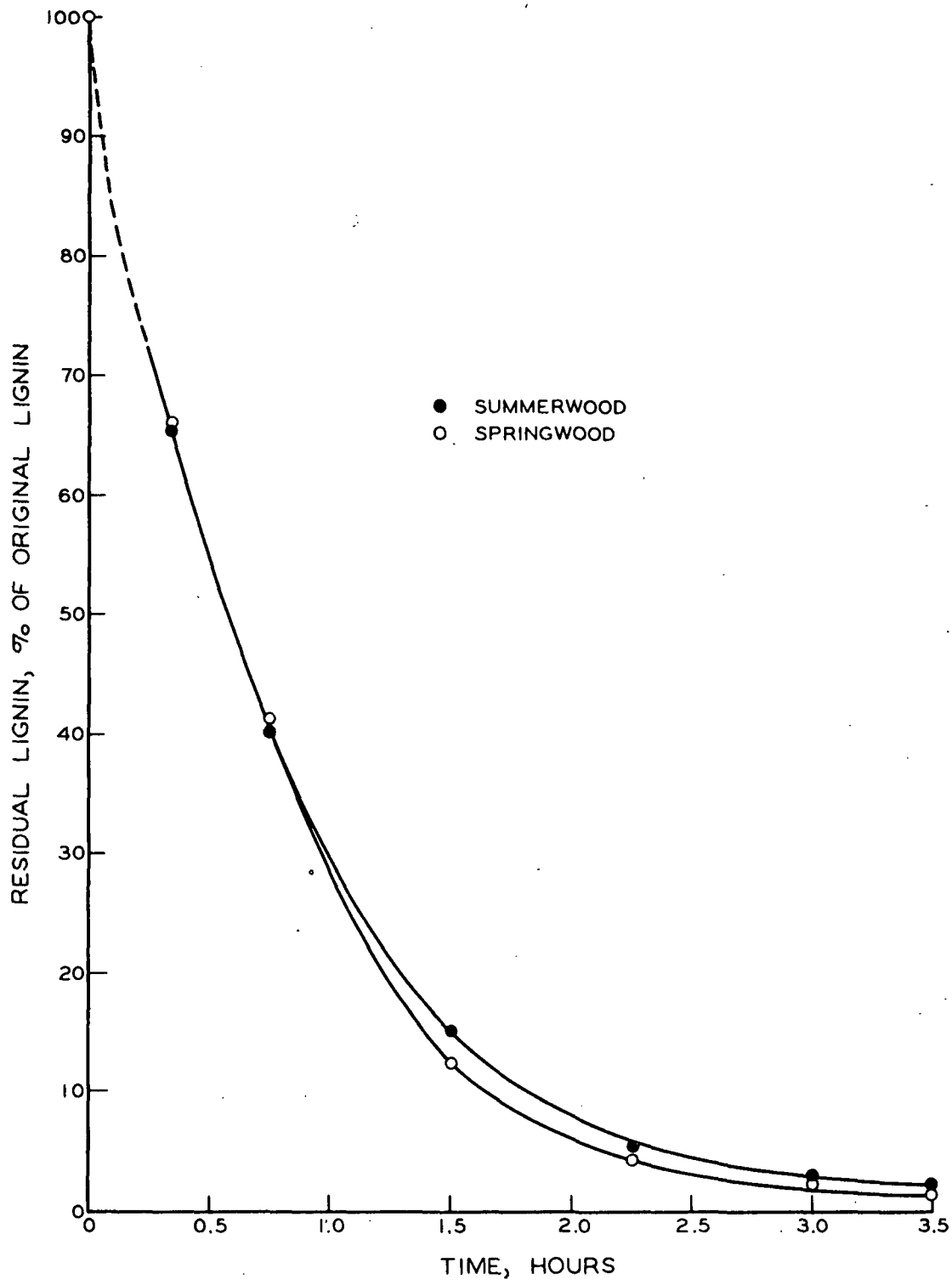

Figure 8. Delignification of Springwood and Summerwood at 196°C.

lignin has decreased to about 70% of its original value, the difference between springwood and summerwood delignification becomes significant.

The question still remains however, just what is the nature of the effect on reaction rate. Since the data which were taken at 175°C. (Fig. 6) are more extensive than those taken at the other temperature levels, they can be examined more carefully to find indications regarding the nature of the diffusion process.

The two delignification curves in Fig. 6 begin to diverge at a residual lignin content of about 70%. One would expect that the divergence of the two curves would continue to increase at longer cooking times. This is not the case, however, After about 4.5 hours of pulping, the difference in lignin contents between the springwood and summerwood appears to begin to decrease. It is interesting to study the curves in terms of the difference in pulping time required to reach any value of residual lignin content. It is found that after the lignin content has decreased to about 40%, the difference in pulping time between the two curves remains constant at about 1 hour until a residual lignin content of about 8% is reached. This observation indicates that a time lag exists between springwood and summerwood delignification during the period that the delignification curves show this parallel nature. In this period, the rates of delignification of springwood and summerwood are equal.

In Fig. 7 and 8 the delignification time lag cannot be shown. This can be the result of a combination of causes. In both cases only limited data are available above a residual lignin content of 30% and it is not believed that such a small amount of data is sufficient to allow an analysis of the diffusion effect. Secondly, it will be shown later that the degree of sulfonation of the lignin is lower throughout most of the cooking cycle at the high temperatures of 184.5 and

196°C. of Fig. 7 and 8. In accordance with the hypothesis of Goring and Rezanowich (24) the lower degree of sulfonation can cause a lowering of the molecular weight of reaction products. This can increase the rate of diffusion of products through the cell wall as suggested by Nokihara, Tuttle, Felicetta, and McCarthy (23) and hence decrease the effect of the summerwood cell wall on the diffusion of reaction products. Finally, Doraiswamy (25) has shown that increasing the temperature of neutral sulfite pulping causes an increase in the extent of carbohydrate degradation. Thus, the rate of diffusion of reaction products through the cell wall can be increased by the more extensive carbohydrate degradation at the temperatures which were used to establish the data shown in Fig. 7 and 8. At this time it cannot be determined which of these causes best explains the results at 184.5 and 196°C.

The effect of physical accessibility of the lignin must not be neglected in the consideration of Fig. 7 and 8. The physical accessibility of the lignin is closely related to the diffusion within the structure of the lignin particle. For this reason the physical accessibility of lignin may be related to the pulping temperature in such a way as to retard the delignification of springwood at high temperatures. This effect will be treated in more detail in the last section of the DISCUSSION.

Below a residual lignin content of 8%, the curves of Fig. 6 appear to diverge and the apparent time lag that was observed in the range of residual lignin contents from 40 to 8% can no longer be shown. This effect may be the result of differences in the concentration of reaction products in the cooking liquor. The liquor-to-wood ratio was 8.8 ml./g. for springwood compared to 6.4 ml./g. for summerwood. Dividing the initial lignin contents of 28.5% for springwood and

25.9% for summerwood by the liquor-to-wood ratio gives values for the maximum lignin concentration in the spent liquor of 0.033 g./ml. for springwood and 0.041 g./ml. for summerwood. These values correspond to the lignin content that the spent liquor would contain if all of the lignin is removed from the wood.

The result of the difference in concentration of reaction products in the spent liquor might account for the apparent divergence of the curves of Fig. 6 at low lignin contents. The residual lignin content of the pulp might be expected to approach a limiting value such that equilibrium is obtained between the lignin retained by the pulp and the lignin in the spent liquor. According to this hypothesis, the residual lignin content of the summerwood will approach a higher value than that of the springwood because of the difference in product concentration in the spent liquor.

The data indicate that although differences exist between springwood and summerwood, these differences appear not to affect the rate of delignification itself but merely show up as a displacement of the lignin vs. time curve along the abscissa as in the parallel portion of Fig. 6. This observation can be explained if the main difference between springwood and summerwood is assumed to be a difference in the diffusional resistance of the cell walls. According to this assumption, the delignification of summerwood would lag the delignification of springwood because of its thicker cell structure. This might result if lignin reaction products are entrapped by the cell wall at the conclusion of a cook and analyzed along with the unreacted lignin.

MECHANISM OF THE DIFFUSION EFFECT

The similarity in the delignification rates of springwood and summerwood might indicate that the rates of hydrolysis and sulfonation reactions are not

greatly affected by the presence of reaction products in the cell wall. It would follow, therefore, that reaction products which are diffusing through the cell wall become immobilized at the time the reaction is stopped. These reaction products are not removed by washing of the pulp but are carried into the lignin analysis. This causes the relationship between the residual lignin content of the wood and time to be affected by the rate of reaction product diffusion.

The product diffusion effect is probably smaller in magnitude for springwood than would be indicated by the difference between cell wall thickness of springwood and summerwood. This results from the predominance of middle lamella lignin in springwood and the greater number of possible diffusion paths associated with the middle lamella lignin.

SULFONATION OF LIGNIN

Any sulfur reactions with the carbohydrate portion of the wood might be expected to be small in comparison with the lignin sulfonation reaction. If a carbohydrate sulfonation reaction does take place, however, as suggested by Kosilova and Nepenin (30), one must be aware of its magnitude before attempting to analyze the sulfonation of lignin. Clearly, if one were to attempt to calculate the lignin sulfur content directly from the raw data without knowledge of an undesirable side reaction such as carbohydrate sulfonation, improper conclusions could result. The effect would be expected to be most serious at very low lignin contents where error introduced by carbohydrate sulfur content would be exceedingly large.

CARBOHYDRATE SULFONATION

In Fig. 9 and 10 the sulfur content is plotted vs. the residual lignin for springwood and summerwood delignification at various temperatures. It will be

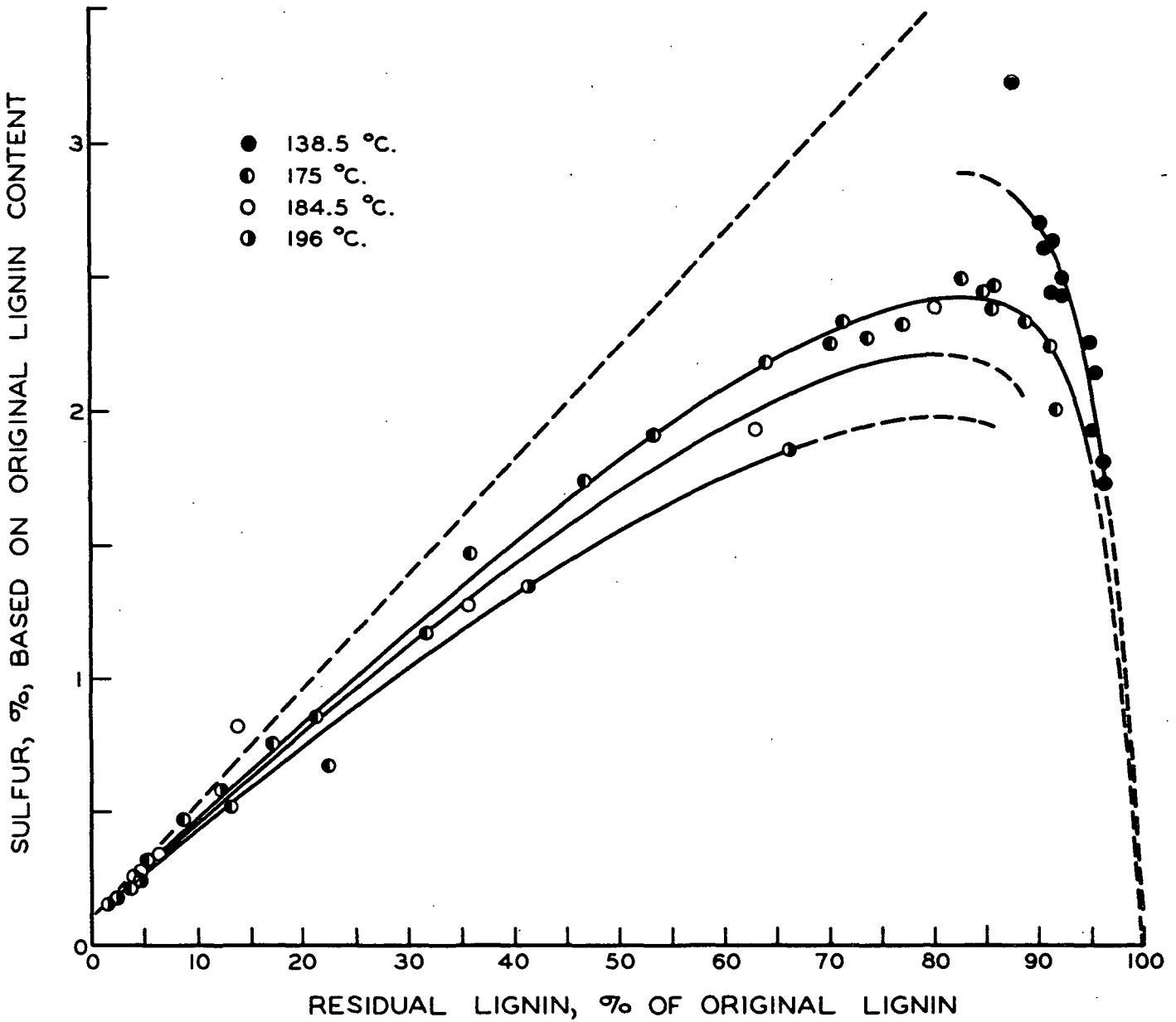

Figure 9. Per Cent Sulfur vs. Residual Lignin Content for Springwood

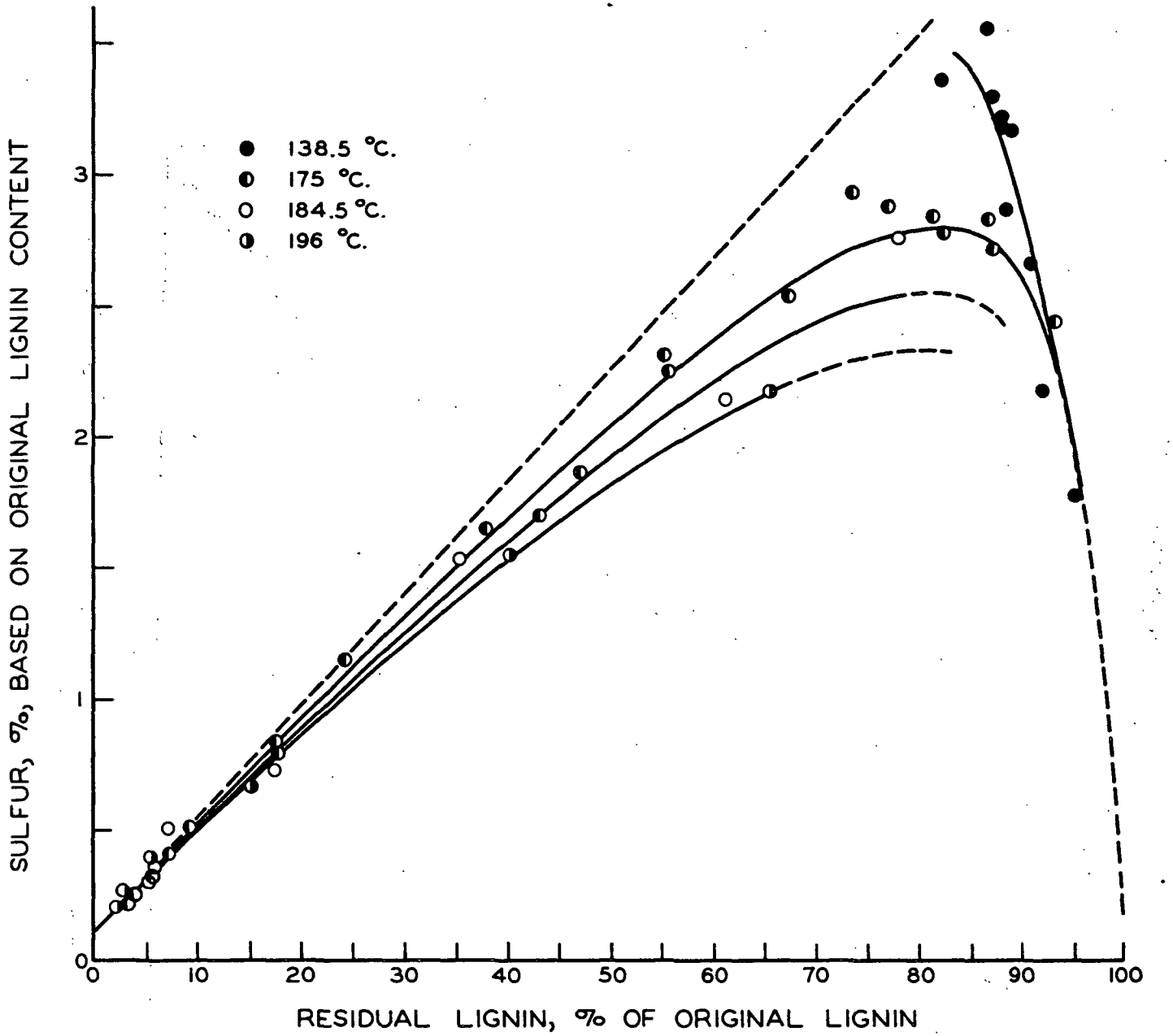

Figure 10. Sulfur vs. Residual Lignin for Summerwood

noted that all of the curves intercept the ordinate at a value of 0.11% sulfur. It would be suggested, therefore, that some of the sulfur has combined with the carbohydrate since one would expect the curves to pass through the origin if this were not the case.

It is unfortunate that no information is available to allow precise calculation of the carbohydrate sulfur content over the entire range of pulping conditions. In order to do so, it would be necessary to know the nature of the reaction and its reaction rate. It can be shown, however, that if we assume the limiting yield of pulp at zero lignin content to be about 40%, the sulfur content of the carbohydrate is about 0.075%. Since the lowest value of original lignin content of the wood is 25.9% for the summerwood, the maximum carbohydrate content is about 74% or less than twice the assumed limiting yield of 40%. It would seem unlikely, therefore, that the sulfur content of the carbohydrate, calculated as a percentage of the original lignin, could reach a value of more than twice its extrapolated value of 0.11%. For this reason, it seems safe to assume that the sulfur content of the carbohydrate is small enough in comparison with the sulfur content of lignin that the results can be examined without difficulty.

DEGREE OF SULFONATION OF THE LIGNIN

The relationship between sulfur content and residual lignin as shown in Fig. 9 and 10 can be used to obtain an estimate of the sulfur content of the last traces of lignin to be removed from the wood. Since a value of lignin content equal to zero would correspond to infinite reaction time, the slope of the sulfur vs. residual lignin curve at zero lignin should be equal to the fraction of sulfur in the final traces of lignin to be removed from the wood. This limiting slope is shown in Fig. 9 and 10 as a straight dashed line. From the

slope of this line a sulfur content of 4.3% is calculated for the last portion of lignin to be removed. Because of the sulfonation of carbohydrate, one might expect this value to be slightly high. As a result of the considerations discussed earlier, however, regarding the magnitude of the carbohydrate sulfur content, it can be shown that it would be necessary to decrease the lignin sulfur content only to about 4.2% to account for the carbohydrate sulfur content. It is believed that since this correction falls within the limits of error of the determination of the limiting slope it can be neglected as being insignificant. The value of sulfur content calculated from the limiting slope of the sulfur vs. residual lignin relationship is in good agreement with the value of about 4.8% found by Goring and Rezanowich (24) for the sulfur content of the lignin obtained from the final fraction in their fractional delignification studies.

EFFECT OF SULFONATION ON REACTION RATE

An examination of the data for the cooks at 175°C. shows that the sulfur content of the pulp, calculated as a percentage of the original lignin, increases during the early portion of the cook, reaches a maximum, and finally decreases as pulping time is increased. English, Green, Mitchell, and Yorston (10) have shown that a relationship of this type indicates that the sulfonation reaction has an effect on the over-all rate of delignification. These workers assumed the rate of hydrolysis to be proportional to the amount of sulfonated lignin. As a result of this assumption, the low degree of sulfonation in the early stage of the cook would inhibit the rate of the hydrolysis reaction.

The effect of sulfonation on the over-all delignification rate can be shown more clearly by an analysis of Fig. 9 and 10. The straight dashed line which was used to determine the limiting sulfur content of the lignin represents the sulfur

content which would be observed for the pulps if all of the lignin was fully sulfonated to 4.3%. The observation is made, however, that the experimental sulfur contents fall below this line and approach it as the residual lignin content is decreased. This indicates that full sulfonation of the lignin is not reached within the time that delignification is taking place. There are two ways in which this can affect the over-all delignification rate. A low sulfur content might decrease the hydrolysis rate by decreasing the number of sites available for hydrolysis to take place. Secondly, it might be expected that the maximum molecular weight of sulfonated lignin that is soluble in sodium sulfite solution would be decreased by a decrease in sulfur content as suggested by Goring and Rezanowich (24). This would make it necessary for partially sulfonated lignin to be degraded by hydrolysis to a greater extent in order to become soluble than would be necessary for fully sulfonated lignin. Thus, the extent of hydrolysis would have to be greater early in the cook in order to liberate lignin. This would cause a corresponding decrease in the over-all reaction rate.

PHYSICAL ACCESSIBILITY

A comparison of Fig. 9 and 10 shows that the summerwood lignin appears to come much closer to being fully sulfonated than the springwood lignin. This effect is believed to be caused by the physical accessibility phenomenon which is treated in a separate section of the DISCUSSION.

ACTIVATION ENERGY OF SULFONATION

The effect of temperature on the relationship between sulfonation and hydrolysis rates is another phenomenon which is shown by Fig. 9 and 10. When sulfur content is plotted vs. residual lignin at various temperatures, a family of curves

results which show that as reaction temperature is increased a lower degree of sulfonation results for any value of residual lignin. This indicates that an increase in reaction temperature causes the percentage increase in the sulfonation rate to be less than the percentage increase in hydrolysis rate. Thus, the ratio of sulfonation rate to hydrolysis rate decreases as temperature is increased. This can be caused either by the effect of temperature on the physical accessibility or by the sulfonation activation energy being lower than the hydrolysis activation energy.

The activation energy of a chemical reaction can be calculated from the Arrhenius equation (31)

$$\ln K = \ln A - E/RT \qquad (1)$$

where K is the reaction rate constant, R is the ideal gas constant, T is the absolute temperature, and A is constant over small ranges of temperature. The term E in the equation is the energy of activation of the reaction. Glasstone, Laidler, and Eyring (31) prefer to define E as the experimental activation energy since it is usually determined from the slope of the $\ln K$ vs. $1/T$ relationship.

Calculation of the activation energy of the sulfonation reaction is difficult because the rate of the sulfonation reaction is high enough that measurement of the rate constant of sulfonation is unwieldy.

It will be assumed that the rate of sulfonation is proportional to some power of the quantity of unsulfonated lignin and that the hydrolysis rate is proportional to some power of the sulfonated lignin. Then, at constant liquor concentration, the rate of change of sulfur content can be expressed as

$$dS/dt = K_s L_u^{\,a} - K_h L_s^{\,b} \qquad (2)$$

where K_s and K_h are the sulfonation and hydrolysis rate constants, L_u is the quantity of unsulfonated lignin, L_s is the amount of sulfonated lignin and a and b are empirical constants. As a result of the complexity of the delignification process, evaluation of all of the terms in Equation (2) presents a difficult problem. The equation can be simplified, however, by a consideration of the initial conditions. At zero time, the amount of sulfonated lignin is zero and the quantity of unsulfonated lignin is equal to the initial lignin content of the wood. Thus, Equation (2) can be reduced to

$$(dS/dt)_o = K_s L_o^{\,a} \qquad (3)$$

where $(dS/dt)_o$ is the initial sulfonation rate and L_o is the lignin content of uncooked wood. Since the value of a is unknown, the sulfonation rate constant cannot be determined. In Fig. 11 and 12 the sulfur content is shown as a function of reaction time for the high-yield springwood and summerwood cooks at 175 and 138.5°C. It will be observed that insufficient data are available to permit calculation of the initial sulfonation rate.

The energy of activation can still be estimated if the assumption is made that the value of sulfur content divided by the time required to reach this sulfur content is proportional to the initial sulfonation rate over a very limited range during the initial rapid rise in sulfur content. Or,

$$S/t_s = D\,(dS/dt)_o \qquad (4)$$

where t_s is the time required to reach the sulfur content S, and D is a proportionality constant. Combining Equations (3) and (4) with Equation (1) gives

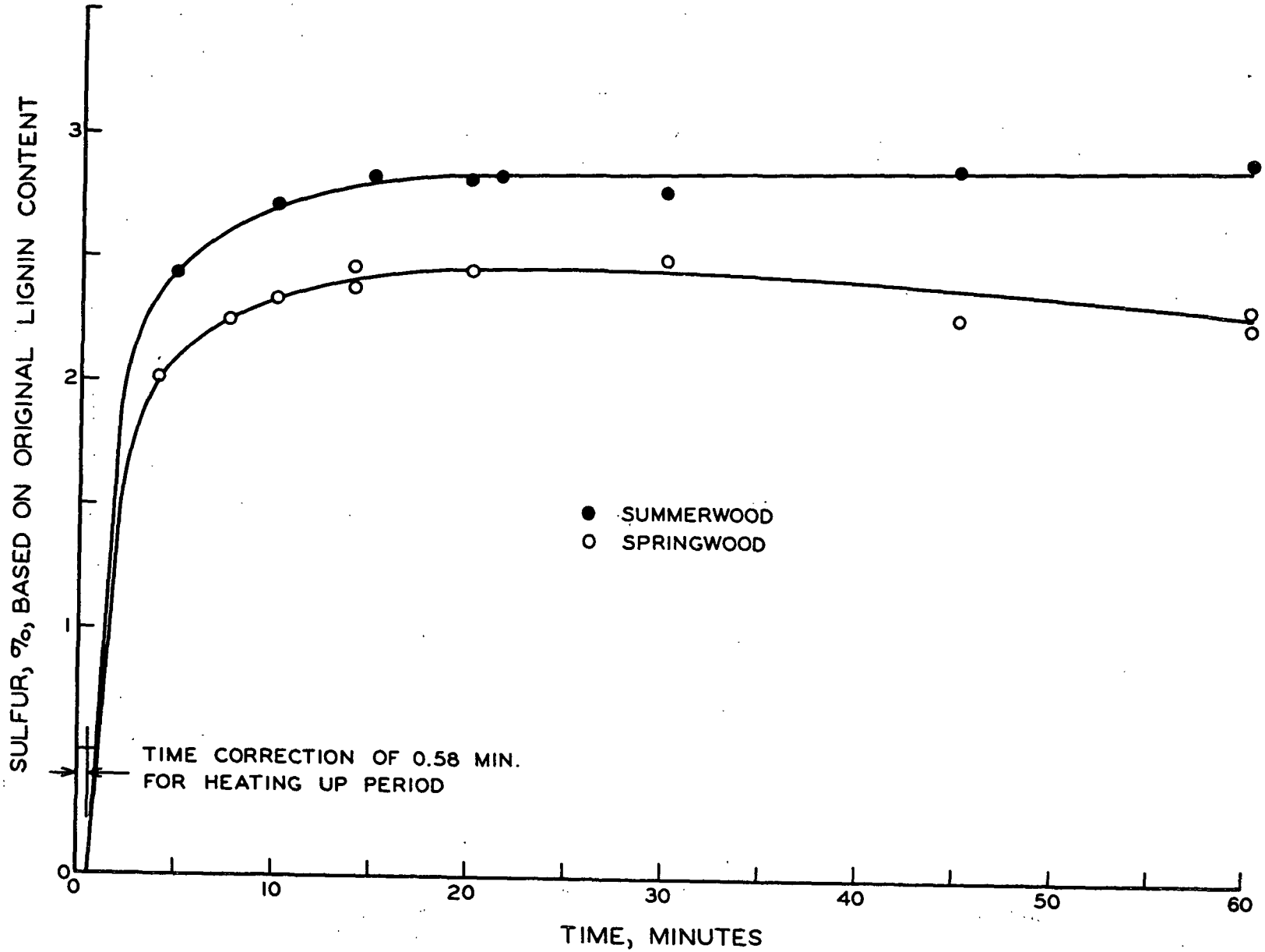

Figure 11. High-Yield Sulfonation of Springwood and Summerwood at 175°C.

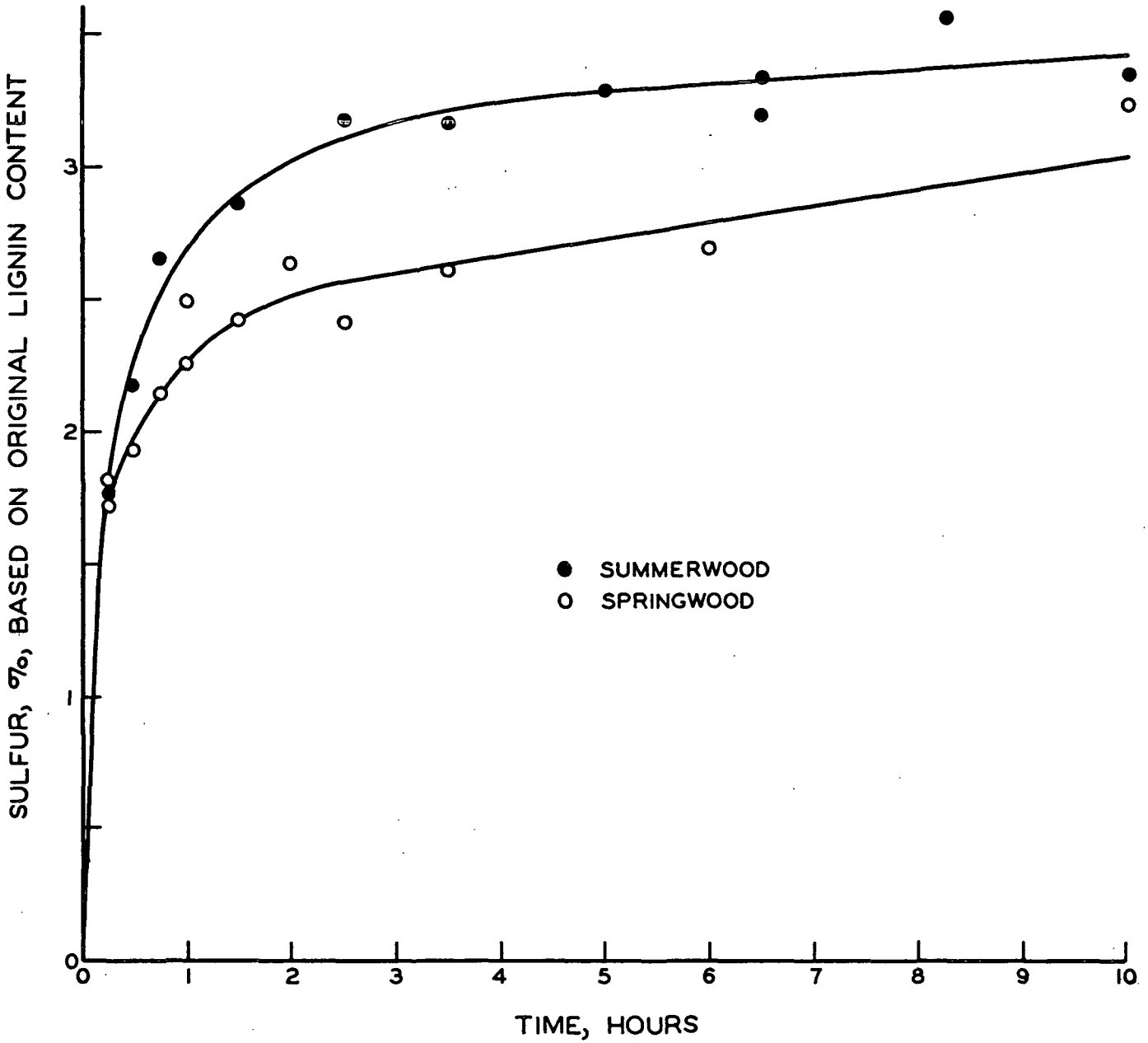

Figure 12. High-Yield Sulfonation of Springwood and Summerwood at 138.5°C. in Unbuffered Liquor

$$\ln (S/t_s) = (\ln A D L_o^a) - E/R T \qquad (5)$$

If the product $\underline{A}\ \underline{D}\ \underline{L_o}^{\underline{a}}$ in Equation (5) can be considered constant, the activation energy can be calculated from the slope of the $\ln(\underline{S}/\underline{t_s})$ vs. $(1/\underline{T})$ relationship.

The activation energy of sulfonation was estimated from the high-yield sulfur data shown in Fig. 11 and 12. The lowest value of sulfur content which was available at both temperatures was used for the determination of $\underline{t_s}$. A sulfur content of 2.0% was used for the springwood calculation and 2.4% was used for the summerwood. As a result of the short duration of the cooks at 175°C., it was necessary to correct the reaction time for this series of cooks by 35 seconds to allow for the heating up time of the reaction. The results of this analysis are shown in Table V. The calculation of the time correction is given in APPENDIX IV.

TABLE V

ESTIMATION OF ACTIVATION ENERGY OF SULFONATION

Temperature, °C.	$\underline{t_s}$, hr.	$\underline{S}/\underline{t_s}$, %/hr.	Activation Energy, cal./g.-mole
Springwood $\underline{S}$ = 2.0%			
175.0	0.057	35.1	22,100
138.5	0.52	3.8	
Summerwood $\underline{S}$ = 2.4%			
175.0	0.067	36.8	21,900
138.5	0.60	4.0	

Clearly, the assumptions used to establish Equation (4) are subject to criticism. The activation energy calculated in this way can be expected to be higher than the true value. This results from the increasing effect of the hydrolysis rate on the determination of S/t_s as reaction time is increased and the fact that hydrolysis has been shown to have a higher activation energy than the sulfonation reaction. However, until the time that more extensive initial rate studies are made, the value of 22,000 cal./g.-mole must be accepted as the best approximation of the activation energy of sulfonation. This value is the average of the two values which were calculated for springwood and summerwood.

HYDROLYSIS OF LIGNIN

The hydrolysis of lignin is a very important step in the delignification process. It provides the necessary degradation of the lignin to form molecules of a low enough molecular weight to dissolve in the cooking liquor. If lignin is considered to be a polymeric substance, one would expect its rate of dissolution to be related to its molecular weight.

THEORETICAL CONSIDERATIONS

Equations (6) and (7) show the rate of dissolution of a linear polymer as a function of its molecular weight. In the derivation of these equations, it has been assumed that secondary valence forces cause an upper limit to the molecular weight of soluble polymer. For this reason, hydrolysis of the polymer must take place in order to produce molecular fragments which are soluble. It has been assumed further, that all possible sites for hydrolysis have an equal probability of being cleaved by the reaction and that the molecular weight of the polymer is uniform before the reaction is started. As a result of these assumptions, the rate of dissolution is given by

$$dP/dt = -k\,P + k\,P_o - k\,P_o\,s_o/C \qquad (6)$$

and

$$s_o/C = (n\,a - 1)\,(a + 1)/(2\,n\,a - a - 1) \qquad (7)$$

for values of n greater than one, where P is the amount of undissolved polymer, P_o is the original quantity of polymer, k is the hydrolysis rate constant, t is time, s_o is the number of reaction sites originally present per gram of polymer, C is the most probable number of cleavages required to dissolve one gram of polymer, n is minimum number of soluble fragments in the original polymer molecule, and a is the number of monomers in the largest soluble fragment. The derivation of these equations is given in APPENDIX V.

The initial dissolution rate is obtained by substituting P_o for P in Equation (6). After rearrangement of terms, this gives

$$(dP/dt)_o/k\,P_o = -s_o/c \qquad (8)$$

where $(dP/dt)_o$ is the initial dissolution rate. An evaluation of the value of s_o/c, therefore, will show the relationship between initial rate and molecular weight. This relationship is shown in Fig. 13 for various values of a. A scale factor of $Z = (a + 1)$ has been used to allow more direct comparison of the curves. The values used in plotting Fig. 13 are given in Table VI.

Figure 13 shows that as n increases from unity the absolute value of the initial dissolution rate decreases rapidly over the first few increments of n. As n is allowed to increase further, however, the effect of molecular weight on the initial rate becomes less severe and the initial rate approaches a value which is one-half of its value when n is equal to one. When n is less than one, hydrolysis is not necessary for the polymer to dissolve. In this case the rate

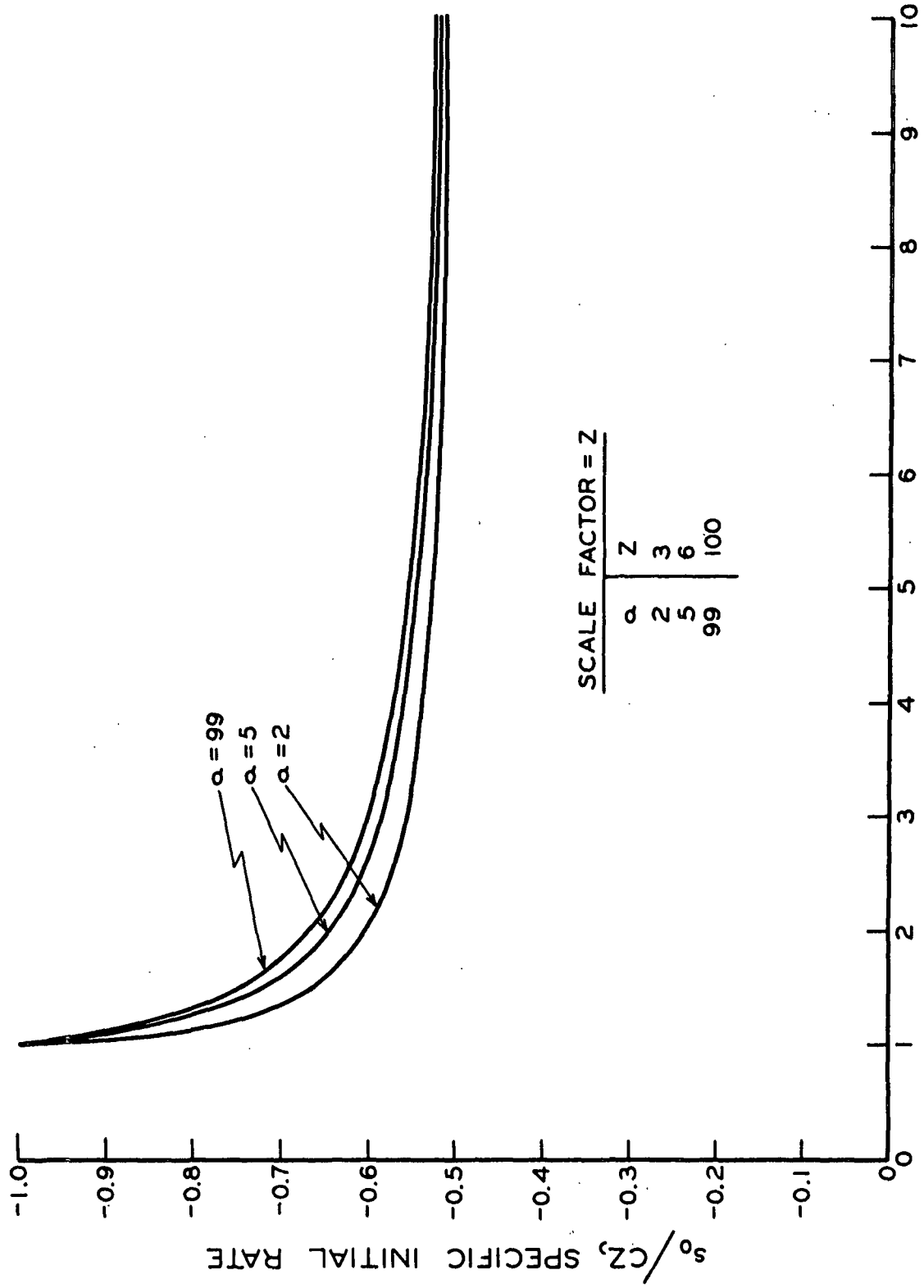

Figure 13. Plot of Equations (7) and (8) for Various Values of a

of dissolution would be governed by other factors but can be expected to be significantly greater than the dissolution rate of a polymer having a value of n greater than one.

TABLE VI

VALUES OF $(d\underline{P}/d\underline{t})_o/\underline{k}\,\underline{P}_o$ AS CALCULATED FROM EQUATIONS (7) AND (8)

n	$a = 2$	$a = 5$	$a = 99$
1.0	-3.00	-6.00	-100.0
1.25	--	-4.85	-83.2
1.5	-2.00	-4.33	-74.8
2.0	-1.80	-3.86	-66.7
3.0	-1.67	-3.50	-59.9
4.0	-1.61	-3.35	-57.1
7.0	-1.56	-3.19	--
10.0	-1.54	-3.13	-52.6
∞	-1.50	-3.00	-50.0

Examination of Equations (6) and (7) shows that as the dissolution process proceeds, the absolute value of the rate decreases. As a result, the effect of molecular weight on the dissolution rate becomes more severe as degradation takes place. It can be shown, however, by an examination of the rate when P is equal to zero, that the ratio of the rate when n is infinite to the rate when n equals one cannot be less than one-fourth. This is the case when a is equal to two. For larger values of a the effect becomes less pronounced and, when a is equal to one, the relationship reduces to a first-order reaction.

The possibility of soluble reaction products being trapped within the structure formed by the insoluble polymer has not been considered in the derivation of

Equations (6) and (7). Clearly, such a phenomenon is possible and would tend to decrease the apparent rate of dissolution. However, the purpose in presenting these equations has been to show the nature of the relationship which can exist between molecular weight and dissolution rate for an ideal system.

One cannot expect an ideal system of the type which has been considered above to be directly applicable to the delignification of wood. Not only is lignin likely to be a branched polymer but it is considered by some to be somewhat cross linked. Goring and Rezanowich (24) for example, speak of a lignin network. Thus, rate expressions based on a linear molecule are useful only to give a qualitative basis upon which delignification rates can be analyzed.

GENERAL NATURE OF THE HYDROLYSIS REACTION

In Fig. 14, 15, and 16 the residual lignin content is plotted on a logarithmic scale *vs.* pulping time for springwood and summerwood delignification at 175, 184.5, and 196°C. In Fig. 14 the delignification curves show an inflection in the high yield range. This is shown more clearly in Fig. 17 where the ordinate and abscissa have been expanded.

The relationship shown by Fig. 14 and 17 suggests that the lignin can be divided into two parts. The first is an easily removed lignin which consists of about 18% of the original lignin and is dissolved at the beginning of the cook. The remaining 82% of the lignin appears to be removed at a much slower rate and will be called the difficultly removed lignin. The easily removed lignin is believed to be the result of the presence of low molecular weight lignin in the wood and the dissolution of the remaining 82% of the lignin is considered to be that part of the reaction in which the rate of hydrolysis is most important. These effects will be discussed later.

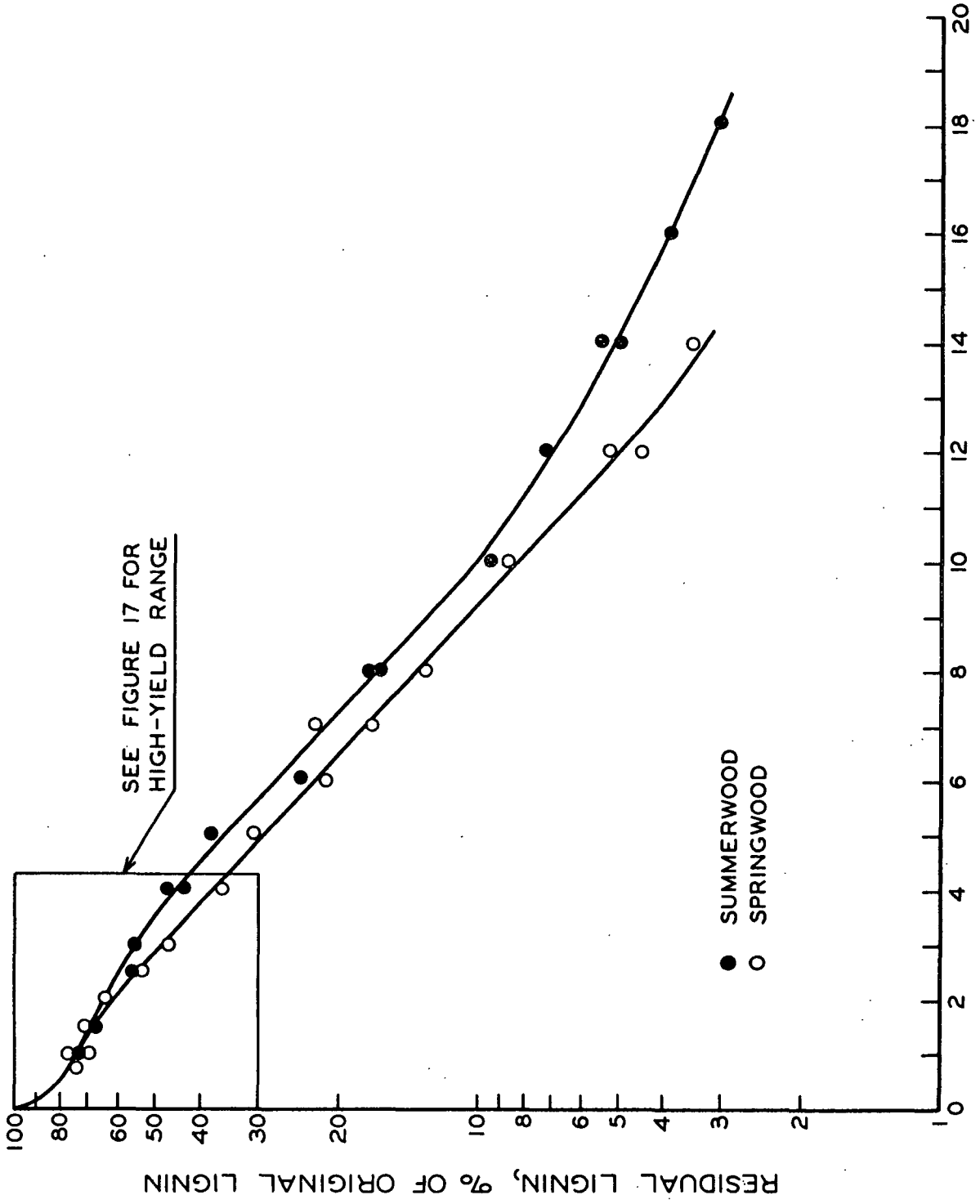

Figure 14. Logarithm of Residual Lignin vs. Time at 175°C.

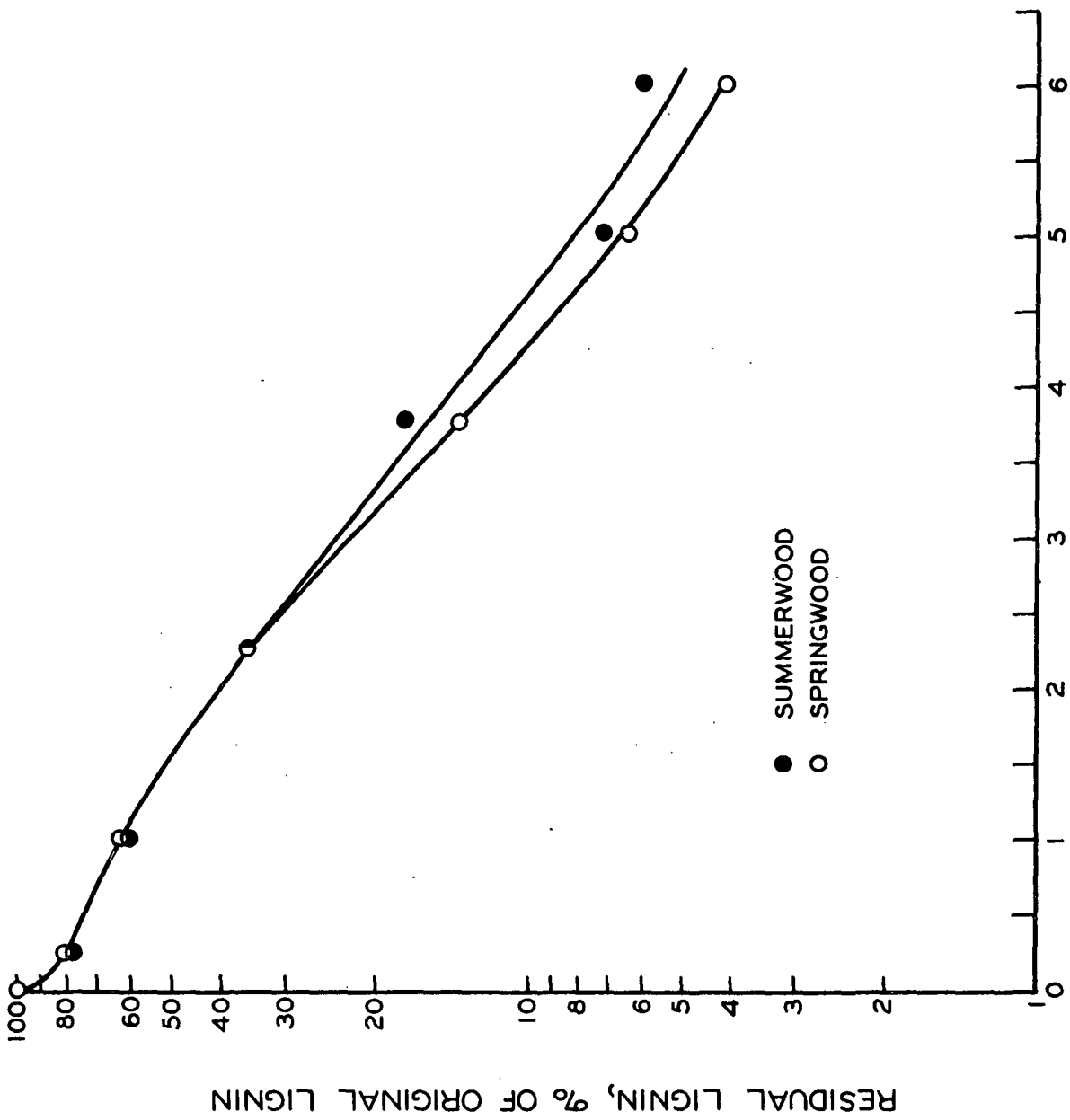

Figure 15. Logarithm of Residual Lignin vs. Time at 184.5°C.

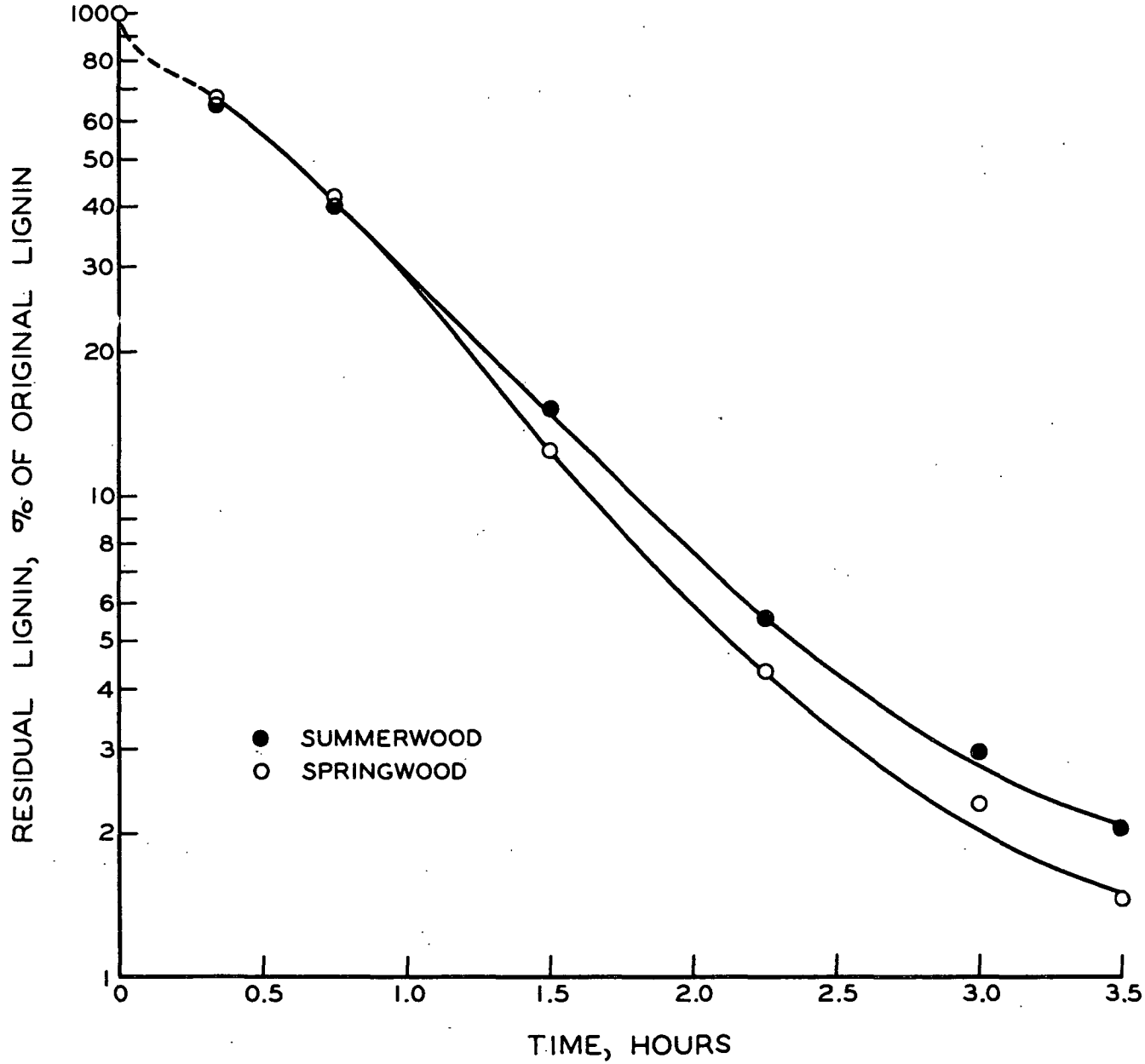

Figure 16. Logarithm of Residual Lignin vs. Time at 196°C.

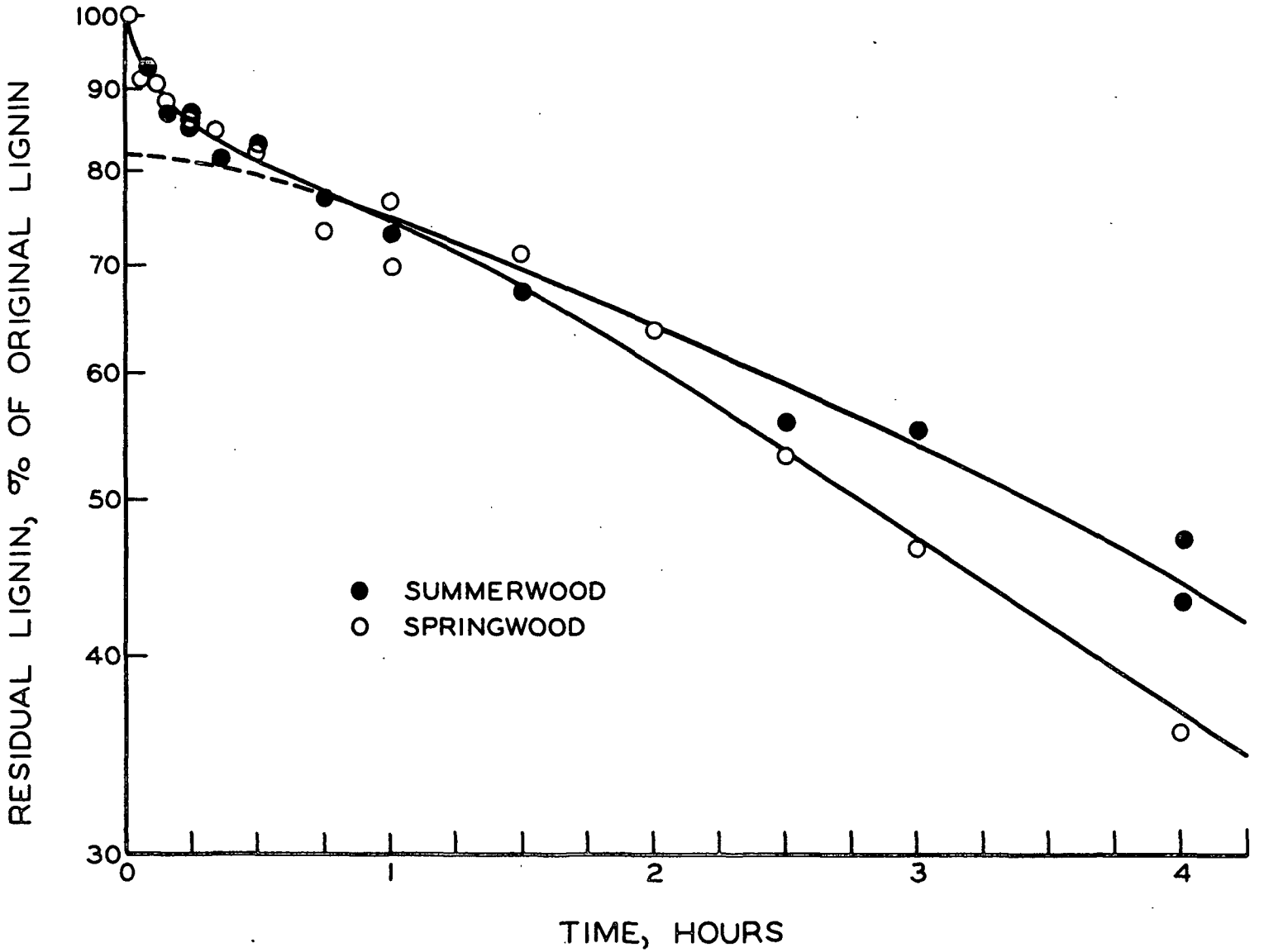

Figure 17. Logarithm of Residual Lignin vs. Time for High-Yield Delignification at 175°C.

Figures 14, 15, 16, and 17 are also useful in showing the effects of sulfonation and product diffusion on the over-all rate of delignification. The difference between the springwood and summerwood delignification curves shows the time lag which is believed to be caused by reaction product diffusion. In addition, the curvature which is observed at short pulping times in these figures for the difficultly removed lignin of springwood is believed to be caused mainly by the effect of the sulfonation reaction.

DIFFICULTLY REMOVED LIGNIN

The method which was used to determine the value of 82% for the difficultly removed lignin results from a consideration of the effect of sulfonation on the initial rate of delignification. Since it is not known whether the lignin must be sulfonated before it can be hydrolyzed or if the hydrolysis reaction is independent of the sulfonation reaction, both cases must be considered. If the sulfonation of lignin must take place before hydrolysis, the initial rate of delignification must be zero. This results from the fact that the initial sulfur content is zero and hence, the initial hydrolysis rate is also zero. On the other hand, if it is assumed that the hydrolysis is independent of the sulfonation reaction, the initial hydrolysis rate would not be zero. A consideration of Equations (7) and (8) and Table VI shows that the value of a, which is the number of monomers in the largest soluble fragment, has a great effect on the initial dissolution rate of the ideal polymer system. Goring and Rezanowich (24) have suggested that the highest soluble molecular weight of lignin can be expected to increase as the degree of sulfonation increases. If this is true, then the value of a will be small in the early stages of delignification because of the low degree of sulfonation. This would result in a lower dissolution rate than in the later stages of delignification when the degree of sulfonation is high. At

initial conditions the degree of sulfonation is zero and one might expect the initial rate of dissolution to be very small. The result of either hypothesis will be a delignification curve on the semilog plot which is concave downward. In Fig. 14 the observation is made that the difficultly removed lignin appears to have a concave downward trend at short pulping times. It is necessary only to extrapolate this curvature back to zero time so that the initial slope is small to obtain an estimate of the quantity of difficultly removed lignin. The dashed line in Fig. 17 represents the extrapolation of the curves for springwood and summerwood back to the initial conditions. Admittedly, this technique is not very precise but it does show the amount of difficultly removed lignin to be approximately 82% of the total lignin in the wood.

EFFECT OF HYDROLYSIS ON REACTION RATE

If the hydrolysis rate is fast enough to have no effect on the reaction rate, sulfonated lignin would be quickly dissolved and removed from the wood. The result would be that the degree of sulfonation of the residual lignin could not reach a very high value. It has already been shown, however, that the degree of sulfonation approaches a value of 4.3%. In addition, the relationship between the sulfur content and residual lignin has been shown to be a function of temperature. For either of these effects to take place it is necessary for a reaction other than sulfonation to affect the over-all rate. The product diffusion step is an unlikely one to be considered since its effect seems to be caused merely by the entrapment of reaction products in the cell wall of the fibers which tends to displace the delignification curve along the abscissa. The only other reaction step which can explain the high degree of sulfonation is the hydrolysis step. Therefore, the rate of hydrolysis must be considered to be slow enough to have

an effect on the over-all delignification rate. This conclusion is supported by the work of others (10, 11). In addition, because of the high degree of sulfonation which is reached, the hydrolysis rate is probably the most important factor in determining the delignification rate of the difficultly removed lignin.

ACTIVATION ENERGY

The delignification of wood has been shown to be a complex process in which at least three of the reaction steps influence the relationship between residual lignin and time. In such a process, one cannot define a single rate constant which will describe the reaction kinetics. In addition, the activation energy of a process which is not controlled by a single reaction step will be some average of the activation energies of those reactions which contribute to the control of the rate.

For a process in which only one reaction step controls the rate, it can be shown that the reciprocal of the time required to reach a given quantity of any of the reacting species, $1/t_x$, is proportional to the reaction rate constant. Thus, $1/t_x$ can be used to determine the activation energy of the reaction. In a process in which the rate is controlled by several reactions, however, this relationship cannot be shown directly because of the dependence of the kinetic relationships on the rates of each of the controlling reactions. Since it is known that the value of $1/t_x$ could be used if any one of the reaction steps controlled the rate, one can imply that this same relationship can be used to obtain the average activation energy when two or more reactions are in control of the over-all rate. This technique has been used by Corey and Maass (5) and Calhoun, Yorston, and Maass (6) to determine delignification activation energies.

The activation energy for the delignification of the difficultly removed lignin has been calculated at several levels of residual lignin content. The results of this analysis are given in Table VII. In addition, the results obtained at a residual lignin content of 10% are shown in Fig. 18 for springwood and summerwood.

TABLE VII

ACTIVATION ENERGY FOR DISSOLUTION OF DIFFICULTLY REMOVED LIGNIN

Residual Lignin, %	$1/t_L$, hr.$^{-1}$			Activation Energy, cal./g.-mole
	175°C.	184.5°C.	196°C.	
		Springwood		
70	0.77	1.63	3.70	31,200
50	0.36	0.66	1.73	28,600
30	0.21	0.39	1.02	28,800
10	0.11	0.24	0.61	34,500
		Summerwood		
70	0.74	1.63	3.70	32,800
50	0.30	0.66	1.73	34,500
30	0.17	0.39	1.02	34,500
10	0.10	0.22	0.56	34,000

The activation energies which are found for the delignification process are in agreement with the conclusion which was made earlier regarding the difference between the activation energies of sulfonation and hydrolysis. If the activation energies in Table VII are considered to be some weighted average of the sulfonation and hydrolysis activation energies, it is clear that the hydrolysis activation energy will be higher than the value of 22,000 cal./g.-mole which was found for the sulfonation reaction.

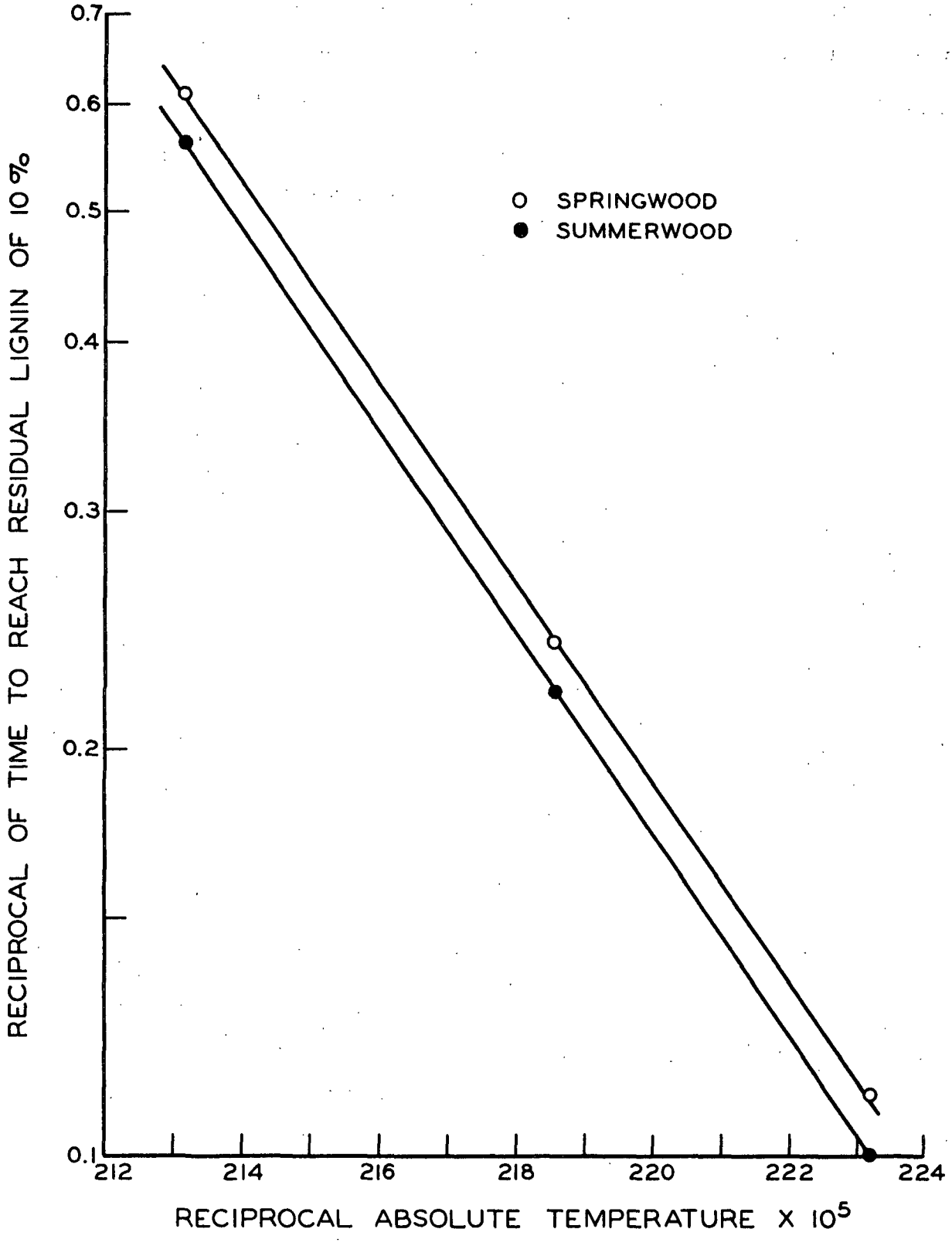

Figure 18. Plot of Arrhenius Relationship for Delignification to 10% Residual Lignin

In general, the activation energies which are presented in Table VII appear to show a slight increasing tendency as the residual lignin content decreases. This is particularly true in the case of the springwood activation energy. A similar observation was made by Goldfinger (7) for acid sulfite pulping. One might expect that an effect of this nature could be caused by the molecular weight distribution of the lignin. However, the effect of molecular weight on the dissolution rate of an ideal polymer system has been shown by Equations (6) and (7) to be small for values of n greater than three or four. Therefore, it is unlikely that molecular weight distribution can affect the activation energy extensively during the period of removal of the difficultly removed lignin. The apparent change in the activation energy with degree of delignification can be explained in terms of the physical accessibility phenomenon and is treated later in the DISCUSSION.

EASILY REMOVED LIGNIN

Approximately 18% of the original lignin of the wood has been shown to be removed at a high rate early in the pulping reaction. In light of the discussion regarding the effect of molecular weight on the dissolution rate of an ideal polymeric system, it would seem reasonable that the easily removed lignin could be lignin which has a low molecular weight. It is also possible, however, that the high rate can be caused by the hydrolysis of extremely labile linkages in the lignin molecule. Should this be the case, however, only a short time would be required for the hydrolysis of labile linkages to produce a molecular weight distribution in the lignin. Thus, the system will be analyzed in terms of a molecular weight distribution in the lignin.

The liquor which was used in the high temperature cooks was a 105 g./ℓ. solution of sodium sulfite having a pH of 9.7. It might be expected that the

liberation of wood acids during cooking would cause a decrease in the pH of the liquor and alter the reaction rate. If such an effect were to take place early in the cook, the easily removed lignin could be affected. Examination of the data for the cooks at 184.5 and 196°C. shows that the spent liquor pH drops initially to a value of about eight and then increases as pulping time is extended until a value between 8.3 and 8.7 is reached at the end of the cook. It would seem necessary, therefore, to examine the effect of pH on the rapidly removed lignin.

EFFECT OF BUFFERING

A series of cooks were made at 138.5°C. to investigate the high yield delignification. Cooks were made on springwood and summerwood using a liquor which was buffered at a pH of 7.6 by the addition of a small amount of acetic acid. In addition, cooks were also carried out using the unbuffered liquor. The results of this experiment are shown in Fig. 19 and 20 where the residual lignin content of the buffered and unbuffered cooks is plotted vs. time for springwood and summerwood. The observation is made that the curves are altered by the buffering but the high initial delignification rate is still present. Examination of the data shows that the spent liquor pH of the buffered cooks remains nearly constant during the reaction. The spent liquor pH of the unbuffered cooks was measured separately and was found to drop to a value of 8.1 after two hours of pulping and decrease further to 8.0 after four hours.

In determining the curve to be drawn through the data points in Fig. 20, the point for the unbuffered cook at 10 hours was not considered. This same relationship is shown in Fig. 23 where the 10-hour summerwood data point has been neglected.

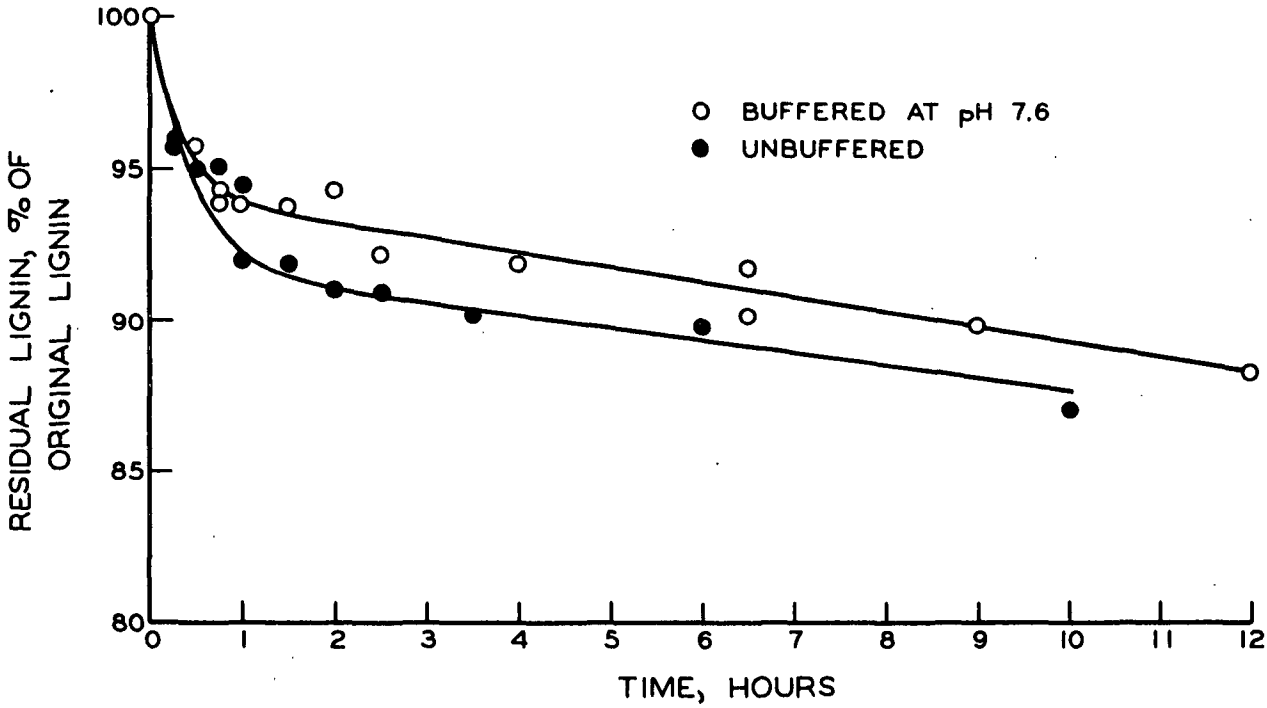

Figure 19. Effect of Buffering on High-Yield Delignification of Springwood at 138.5°C.

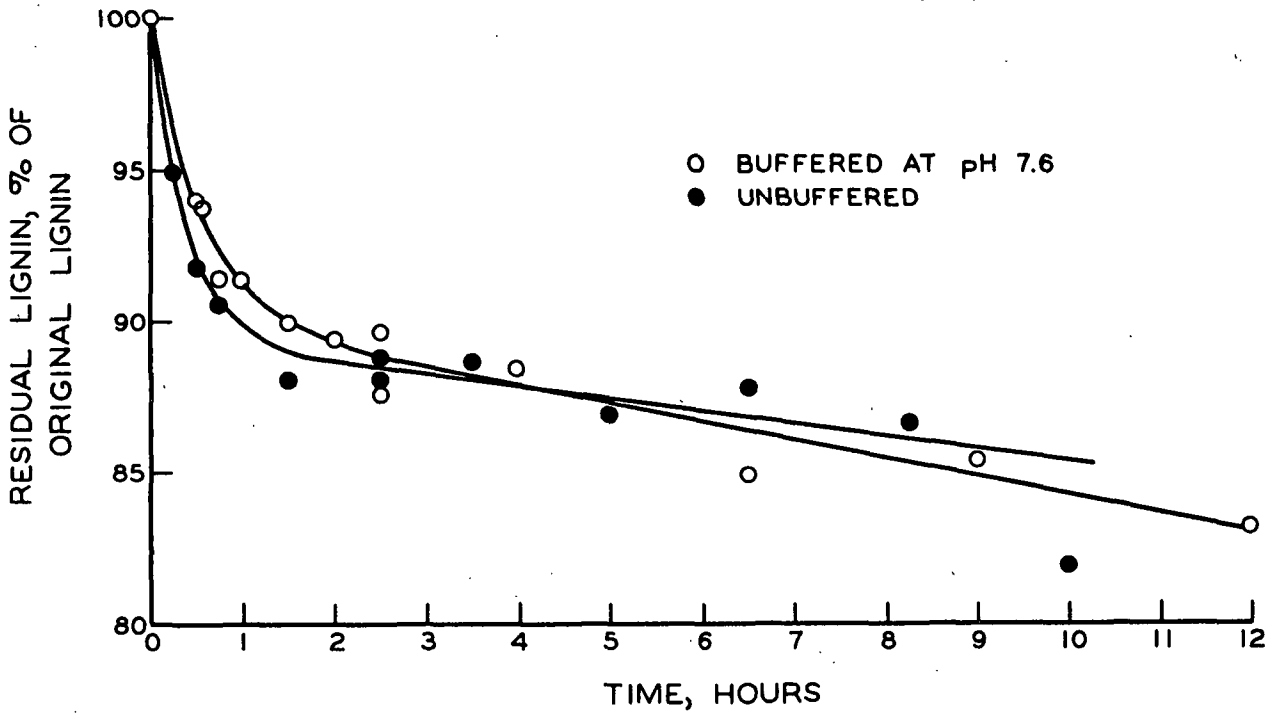

Figure 20. Effect of Buffering on High-Yield Delignification of Summerwood at 138.5°C.

EFFECT OF DIOXANE PRETREATMENT

An experiment was performed in which a sample of springwood was extracted with boiling dioxane containing 0.12% hydrogen chloride for one hour in an attempt to remove the low molecular weight fraction of the lignin. This treatment removed 10% of the lignin from the wood. The dioxane-extracted wood was then cooked in buffered liquor at 138.5°C. The results of this experiment are shown in Fig. 21 where the delignification of dioxane-extracted springwood is compared with the delignification of a normal springwood sample. The data show that the percentage of lignin which is removed at the high initial rate has been significantly reduced by the extraction. The same result would be expected if the high initial rate is caused by either low molecular weight lignin or labile linkages.

The starting point for the delignification of the dioxane-extracted sample was at a value of 90% of the lignin present in unextracted wood. This value of 90% is below the value which is obtained by extrapolating the low-rate portion of the high-yield delignification curve of the normal wood back to zero time. The assumption is made, therefore, that the high initial delignification rate which is observed for the dioxane-extracted sample resulted from a degradation of the lignin by the treatment with the acidified dioxane solution.

An attempt was made to measure the intrinsic viscosity of lignin prepared by fractional extraction of springwood with acidified dioxane. Large losses of lignin occurred during the purification of the sample and the experiment was unsuccessful.

ACTIVATION ENERGY OF INITIAL RATE

If the lignin which is removed at a high rate in the beginning of the cook requires no hydrolysis but dissolves immediately upon sulfonation, its rate of

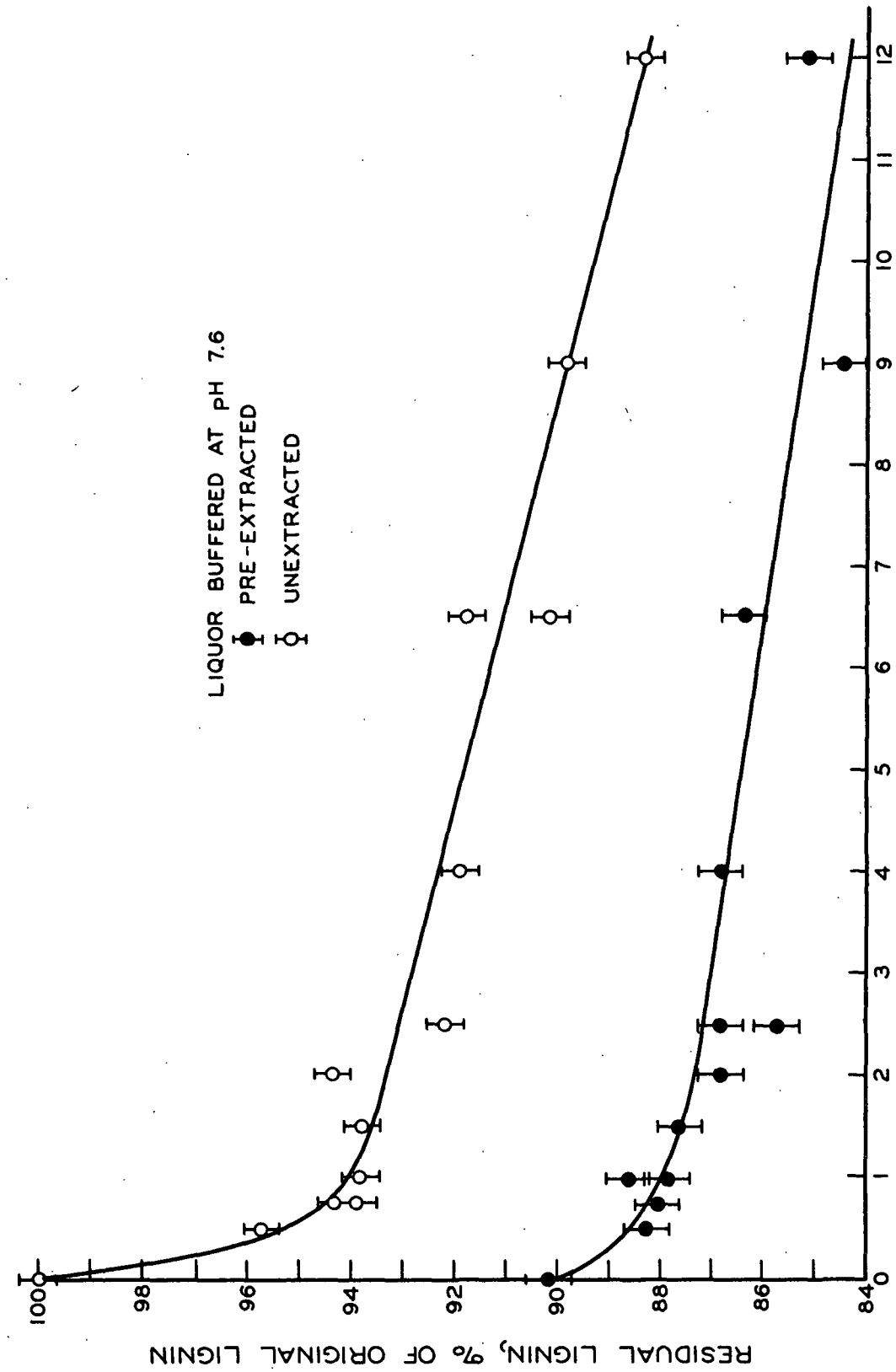

Figure 21. Effect of Dioxane Pre-extraction on High-Yield Delignification of Springwood at 138.5°C.

removal can be expected to be controlled by the rate of sulfonation. This would result in an initial activation energy of delignification which is equal to the activation energy of the sulfonation reaction.

The activation energy has been calculated from the initial delignification rates at 138.5 and 175°C. The results are shown in Table VIII. The initial rates were determined from the high-yield delignification curves shown in Fig. 22 and 23. A correction of 35 seconds has been made for the heating up time of the cooks at 175°C.

TABLE VIII

INITIAL RATE ACTIVATION ENERGY

Temperature, °C.	Initial Rate, %/hr.	Activation Energy, cal./g.-mole
	Springwood	
175.0	173	22,600
138.5	18	
	Summerwood	
175.0	173	20,600
138.5	22	

The estimated activation energy of the initial delignification agrees well with the estimated sulfonation activation energy of 22,000 cal./g.-mole. This suggests that the initial rate of delignification is controlled by the rate of the sulfonation reaction and supports the hypothesis that the high initial delignification rate results from the removal of low-molecular weight lignin or the hydrolysis of labile linkages. The initial rate activation energy will be taken as 21,600 cal./g.-mole which is the average of the two values determined above.

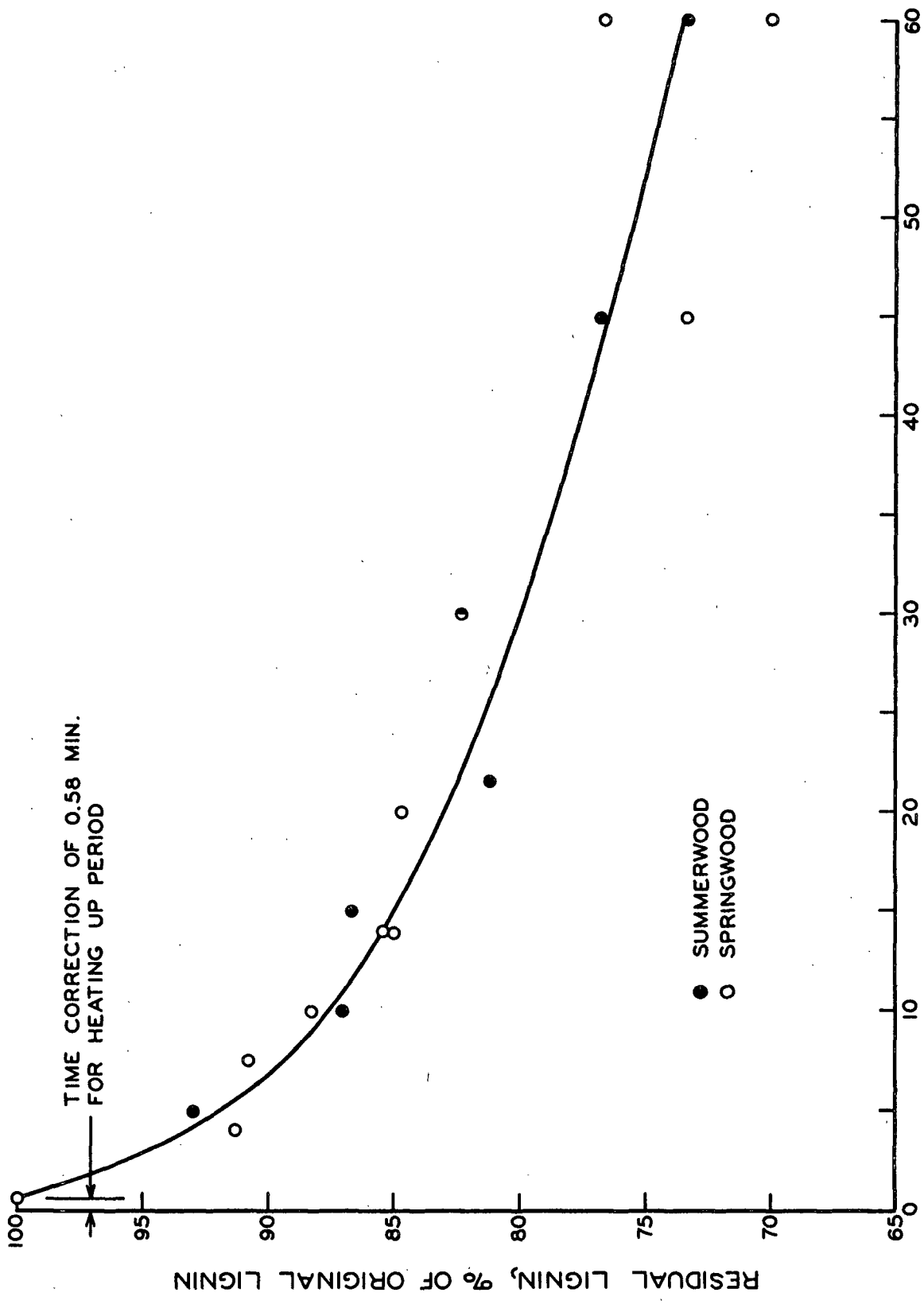

Figure 22. High-Yield Delignification of Springwood and Summerwood at 175°C.

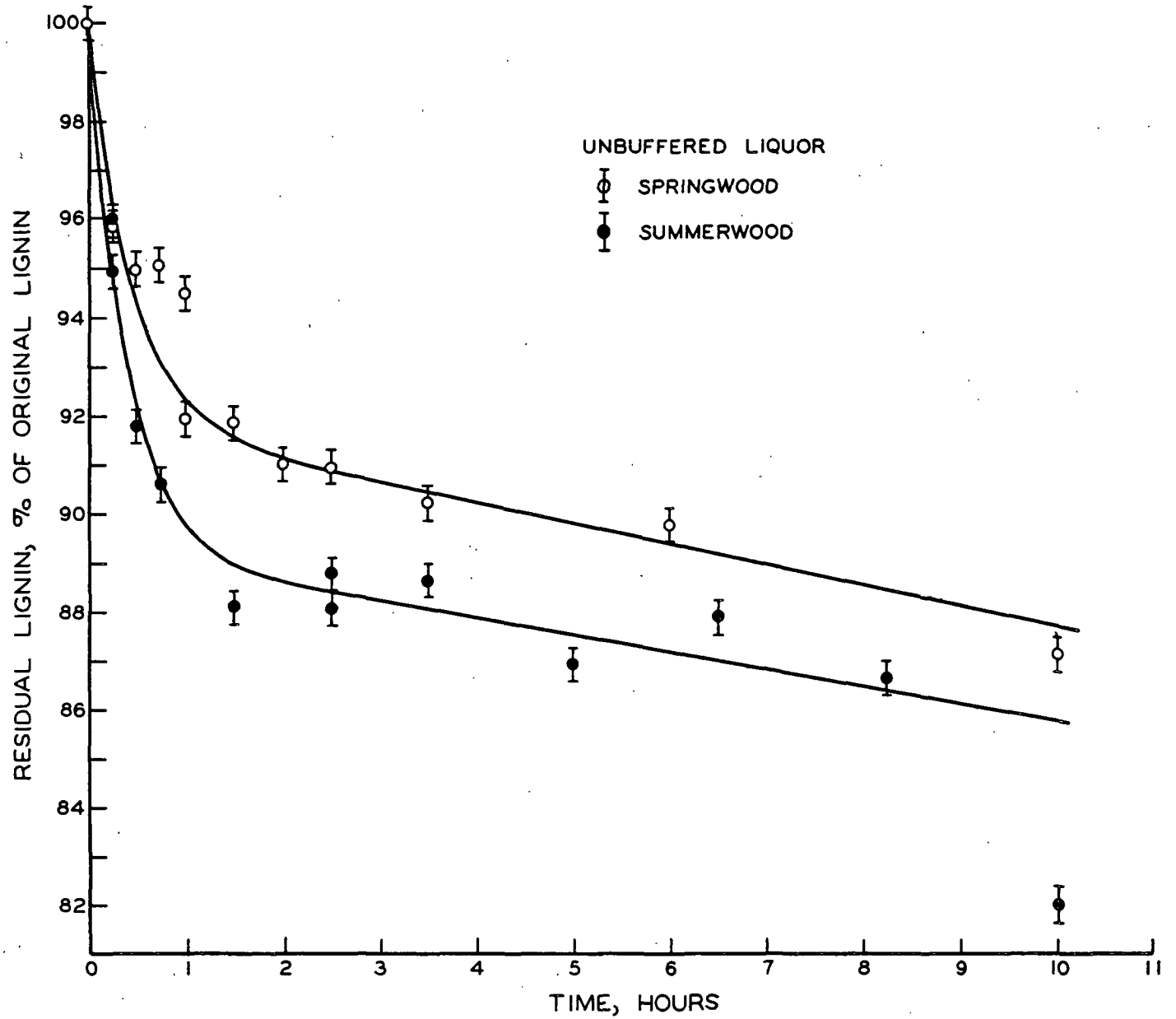

Figure 23. High-Yield Delignification of Springwood and Summerwood at 138.5°C.

THE ROLE OF MOLECULAR WEIGHT

It will be noted that if the low-rate portions of the curves in Fig. 19 and 20 are extrapolated to zero time, an intercept is obtained which is higher than the value of 82% which was obtained from the data at 175°C. It would appear that the easily removed lignin can be further divided into two parts. One of these seems to be more highly soluble than the other as evidenced by the very sharp change in delignification rate after about one hour of pulping at 138.5°C.

It is possible to explain this result in terms of a hypothetical molecular weight distribution of the lignin. If lignin can be considered to be capable of forming cross links, one would expect that most of the lignin would have a network structure. During the formation of this structure it is conceivable that molecules of a low molecular weight can become immobilized and will be unable to form the necessary cross links to become a part of the network. Therefore, the lignin network would be interspersed with smaller molecules of lignin which are slightly branched or linear. These smaller molecules would be expected to have a molecular weight distribution of their own. A structure of this type can be expected to show at least three different delignification rates.

Among the molecules of low molecular weight, some might be small enough to dissolve immediately upon sulfonation without the need for hydrolysis to take place. These molecules would be analogous to the ideal polymer which was considered earlier for the case in which the value of $\underline{n}$ is less than one and can be expected to have a high dissolution rate.

The second portion of the low molecular weight lignin would be large enough to require hydrolysis in order to be dissolved. This would result in a lower dissolution rate as in the case of the ideal polymer where the value of $\underline{n}$ is greater than one.

For the cross-linked part of the lignin structure, one can expect that a greater number of molecular cleavages will be required to liberate a soluble fragment than for linear or slightly branched molecules. Therefore, the rate of dissolution of the cross-linked lignin would be lower than that of the second portion of the low-molecular weight lignin. Part of the network structure can exist as free branches of the network structure or as long chains between points of cross linking. These branches would be expected to react in the same way as the second portion of the low-molecular weight fraction and would dissolve at a similar rate.

It must also be considered that the inability of the low-rate portion of the high-yield delignification curves to extrapolate to a value of 82% can be caused by soluble molecules which are trapped within the structure of the insoluble lignin. This phenomenon can be expected to reduce the rate of delignification and is discussed below.

PHYSICAL ACCESSIBILITY

In the beginning of the Discussion, it was stated that the physical accessibility of lignin would be defined to include the immobilization of reaction products by the lignin structure and the possible existence of a reaction zone on the surface of lignin particles. These two phenomena were combined because either one would have a retarding effect on the delignification reaction and separation of these effects would be difficult in a kinetic study.

It was mentioned earlier that a high percentage of the lignin of summerwood is situated in the cell walls of the fibers. In the case of springwood, however, a high percentage of the lignin is contained in the middle lamella. One can

expect the spatial concentration of cell wall lignin to be less than the concentration of lignin in the middle lamella. It is possible, therefore, that the particle size of the middle lamella lignin is greater than the particle size of cell wall lignin. If this is true, middle lamella lignin will be less accessible than cell wall lignin and one can expect any effects caused by physical accessibility to be greater in magnitude for springwood than for summerwood. Evidence of the physical accessibility is found in the work of Bixler (15) and Bucher and Widerkehr-Scherb (16) where the portion of the middle lamella which exists in corners where three or more cells come together was found to require a longer time to dissolve than the remainder of the middle lamella.

In the discussion of the sulfonation reaction, it was mentioned that the summerwood appears to sulfonate more efficiently than the springwood. This effect is shown in Fig. 24, 25, and 26 where the relationship between the sulfur content and residual lignin is given for springwood and summerwood at 175, 184.5, and 196°C. The degree of sulfonation of the summerwood is seen to be greater in all three cases and indicates that the summerwood has a higher accessibility to sulfonation than springwood.

Both portions of the physical accessibility phenomenon are related to diffusion within the structure of the lignin particle. However, the depth of the reaction zone can also be related to diffusional effects outside the physical bounds of the particle itself since it is associated with the diffusion rate of cooking chemical into the lignin structure. Initially, the lignin particle is surrounded by cooking chemical of high concentration. As the reaction begins, a concentration gradient is set up in the liquor surrounding the particle. If the chemical reaction is fast as in the case of the sulfonation of lignin, the

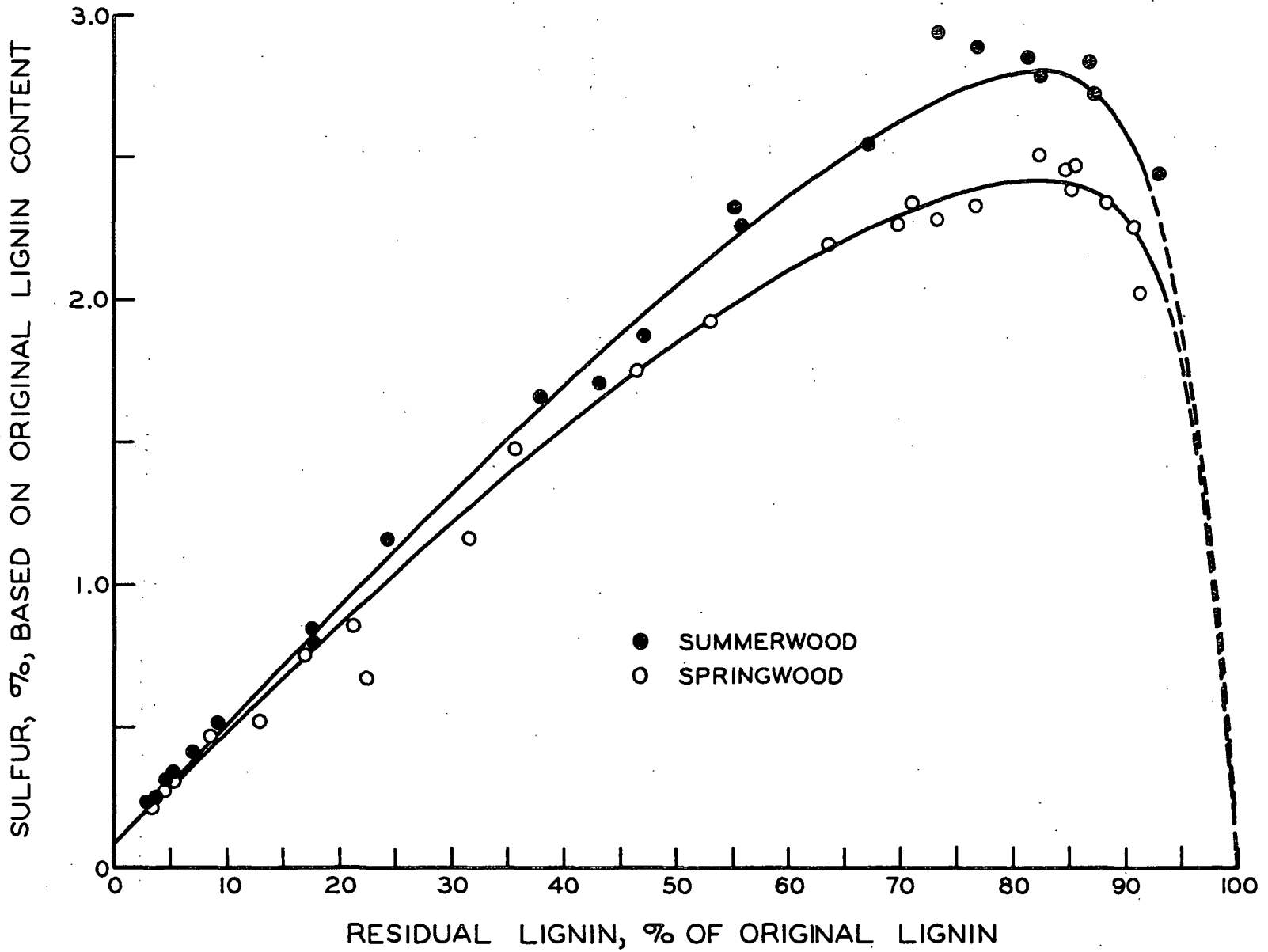

Figure 24. Sulfur vs. Residual Lignin for Springwood and Summerwood at 175°C.

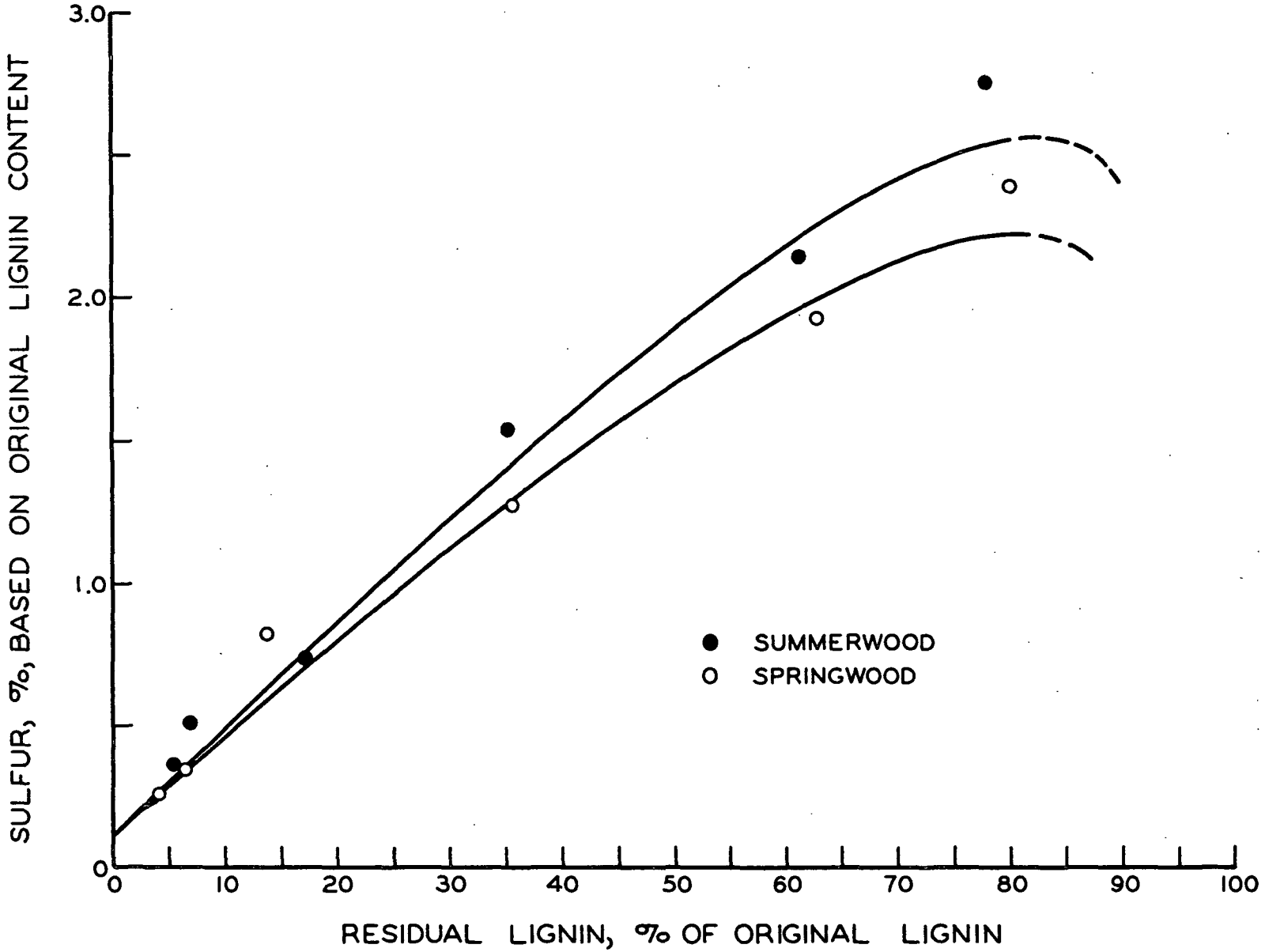

Figure 25. Sulfur vs. Residual Lignin for Springwood and Summerwood at 184.5°C.

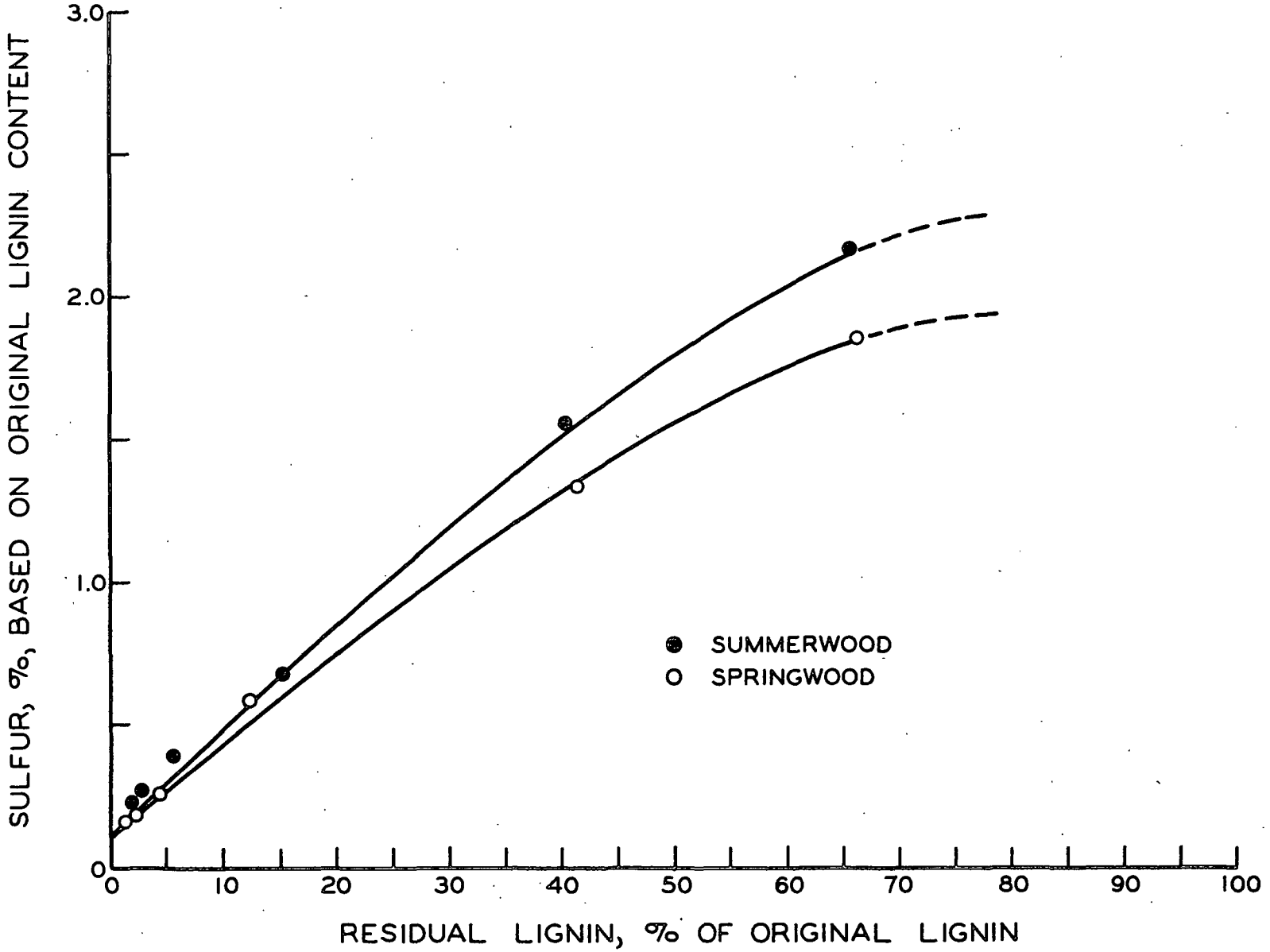

Figure 26. Sulfur vs. Residual Lignin for Springwood and Summerwood at 196°C.

rate of diffusion of active chemical to the particle may begin to play an important role in determining the sulfonation rate.

If the activation energy for the diffusion of cooking chemical into the lignin particle is less than the delignification activation energy, the degree of penetration of cooking chemical into the lignin particle at any given residual lignin content will be lowered by an increase in reaction temperature. As a result of this, the apparent depth of the reaction zone on the surface of the lignin will be decreased by an increase in temperature and the degree of sulfonation and the rate of delignification will be adversely affected. The effect of temperature on the degree of sulfonation of the lignin which was shown in Fig. 9 and 10 does not show this relationship clearly because at least part of the temperature effect results from the difference between the sulfonation and hydrolysis activation energies.

As the delignification of wood proceeds, the particles of lignin decrease in size. Therefore, the physical accessibility phenomenon will be most pronounced at the beginning of the reaction and, as the extent of delignification increases, the reaction will become increasingly homogeneous in its properties. The data indicate that summerwood has a higher physical accessibility than springwood. Therefore, any effect on the physical accessibility caused by temperature changes should be smaller for summerwood than for springwood because the summerwood delignification will acquire homogeneous characteristics at an earlier stage of the reaction than the springwood.

In the discussion of Fig. 6, it was shown that the difference between the delignification curves for springwood and summerwood could be explained on the basis of reaction product diffusion through the summerwood cell wall. Still, the

observation was made that at the higher delignification temperatures of Fig. 7 and 8 separation of the springwood and summerwood delignification curves did not take place until very late in the reaction. This result can be explained if the physical accessibility of lignin is decreased by increasing the reaction temperature. Since the springwood can be expected to have a greater dependence of physical accessibility on temperature, its delignification will be retarded more by a temperature increase than the summerwood. This will cause the difference between the delignification curves to decrease. At very low lignin contents, the springwood particle size decreases to a point where physical accessibility is no longer important and the curves begin to separate.

The tendency for the delignification activation energy of the difficultly removed lignin of springwood to increase as the residual lignin content decreases also supports the argument in favor of the physical accessibility phenomenon. In Fig. 18, the Arrhenius plot for a residual lignin content of 10% shows good agreement with a straight line for both springwood and summerwood. However, at higher values of residual lignin content, the Arrhenius plot for summerwood gave good straight lines, whereas for springwood, curves were obtained which were always concave upwards. The curvature of the relationship for springwood at the higher residual lignin contents indicates that the value which was used to approximate the delignification rate ($1/\underline{t}_{\underline{L}}$) was too low at the two higher temperatures and points to the transition of the reaction from homogeneous to heterogeneous characteristics as temperature is increased. Conversely, the linearity of the summerwood Arrhenius relationship indicates that homogeneous characteristics prevail over the temperature range which was studied. The similarity of activation energy together with the linearity of the Arrhenius plot for both springwood and summerwood at a residual lignin content of 10% suggests that, at this low lignin

content, physical accessibility of the springwood has ceased to be an important variable.

The Arrhenius relationship for summerwood at a residual lignin content of 70% did not show this effect. Instead, a curve was obtained which was concave downwards. However, at this high value of lignin content the determination of reaction time is subject to considerable error and the lack of agreement is not necessarily a real effect.

The activation energy of the springwood delignification was measured by the arbitrary method of fitting a straight line to the data passing through the point at 175°C.

It has been mentioned earlier, that because of the high degree of sulfonation of the lignin, the hydrolysis reaction is believed to be the major rate-determining step of the reaction. To acquire an estimate of the activation energy of hydrolysis without interference caused by physical accessibility effects, the three highest activation energies of summerwood delignification and the highest value for springwood delignification have been averaged. The estimate of the hydrolysis activation energy therefore, is 34,400 cal./g.-mole.

The data in Fig. 23 show the lignin content of the summerwood to be lower than that of the springwood after the high initial rate period has been completed. This effect is contrary to what has been observed for pulping in the low-yield range where the diffusion of reaction products is believed to cause the residual lignin content of the summerwood to be higher than the springwood. The difference between the residual lignin contents of springwood and summerwood in the high-yield range of pulping is believed to be caused by the physical accessibility phenomenon.

Early in the cook the effects caused by physical accessibility are most severe and, if the high initial rate period is caused by the removal of low molecular weight lignin, the effects caused by diffusion through the cell wall will be small at the beginning of the cook. Thus, the magnitude of the effects caused by physical accessibility and reaction product diffusion will change in their relative importance as the reaction proceeds. This explains why the relationship shown by Fig. 23 appears to contradict the findings regarding the effect of reaction product diffusion.

In the high-yield data at 175°C., which are shown in Fig. 22, no difference can be found between the accessibility of springwood and summerwood. The data which were examined at 138.5°C., however, had a range of residual lignin contents from 100% to a value of 86%. Within this same range of residual lignin contents at 175°C., however, only a few data points are available. In addition, as a result of the very short pulping times which were necessary to collect these data at 175°C., the experimental error is probably greater than for the low-temperature cooks. It is not surprising, therefore, that separation of the delignification curves is not observed in this case.

SUMMARY AND CONCLUSIONS

A study was conducted on the kinetics of neutral sulfite delignification of loblolly pine. Emphasis was placed on the effects which the morphological characteristics of springwood and summerwood have on the over-all delignification rate. Information has been obtained to show the relative effects of sulfonation, hydrolysis, and product diffusion on the reaction rate. In addition, the effects of molecular weight distribution of the lignin and its physical accessibility are discussed.

EXPERIMENTAL FINDINGS

1. The dissolution of lignin can be divided into three periods each of which is characterized by a different reaction rate. The first and second periods account for the first 18% of the lignin to be removed from the wood and are referred to collectively as the easily removed lignin. The rate of delignification during the first period is considerably higher than that of the second period and will be called the period of high initial rate. The third delignification period corresponds to the removal of the last 82% of the lignin and is the slowest of the three periods. This portion of the lignin is called the difficultly removed lignin.

2. The amount of lignin which is removed during the high initial rate period is greater for summerwood than for springwood.

3. The amount of lignin dissolved during the high initial rate period is less when cooking is carried out in a liquor which has been buffered at a pH of 7.6 than when an unbuffered liquor having an initial pH of 9.7 is used.

4. The high initial rate lignin of springwood is affected more by buffering of the liquor than that of the summerwood.

5. Extraction of springwood with acidified dioxane before cooking in buffered liquor has been shown to reduce the amount of lignin removed during the high initial rate period.

6. The amount of easily removed lignin (first and second periods) appears to be the same for springwood and summerwood.

7. The activation energy of the sulfonation reaction has been shown to be less than that of the hydrolysis reaction.

8. The activation energy of sulfonation has been estimated from the initial sulfonation rate and is approximately 22,000 calories/g.-mole.

9. The activation energy of hydrolysis has been estimated to be 34,400 cal./g.-mole from the delignification activation of the difficultly removed lignin.

10. The activation energy during the high initial rate period is estimated at 21,600 cal./g.-mole. The agreement between this value and the sulfonation activation energy indicates that sulfonation controls the rate of removal of the easily removed lignin.

11. The data indicate that the rate of sulfonation is low enough to affect the over-all delignification rate during the dissolution of the difficultly removed lignin.

12. The data indicate that the hydrolysis is the most important factor in determining the rate of removal of difficultly removed lignin.

13. Summerwood delignification lags the springwood delignification during the dissolution of the difficultly removed lignin.

14. The rate of sulfonation of summerwood is greater than that of springwood. This results in the summerwood lignin having a higher degree of sulfonation during most of the cook. The degree of sulfonation of both springwood lignin and summerwood lignin however, approaches a sulfur content of approximately 4.3% toward the end of the cook.

15. An incidental but interesting result is that there appears to be a slight uptake of sulfur by the carbohydrate portion of the wood. A rough estimate places the sulfur content of the carbohydrate at approximately 0.075%.

PROPOSED HYPOTHESIS OF DELIGNIFICATION MECHANISM

Goring and Rezanowich (24) consider the limiting molecular weight of soluble lignosulfonates to be related to the degree of sulfonation and, as the degree of sulfonation of the lignin increases, the larger fragments of the lignin network produced by the hydrolysis become soluble. These workers also consider highly cross-linked lignin to have a low dissolution rate.

As a result of the reaction phenomena which were observed during this investigation, this hypothesis is extended to include the effects of molecular weight distribution, reaction product diffusion, and physical accessibility of the lignin on the delignification rate. The hypothesis is summarized below.

The neutral sulfite delignification of wood takes place by means of simultaneous sulfonation and hydrolysis of the lignin polymer. Certain molecules of the lignin are of a molecular weight that is small enough to be dissolved as soon as sulfonation takes place. No hydrolysis of these small molecules is

necessary and the dissolution rate, therefore, is controlled by the sulfonation rate. The remainder of the lignin requires hydrolysis to break down the lignin into soluble fragments. This high molecular weight lignin has a low dissolution rate which is governed primarily by the rate of hydrolysis.

Lignin can be considered to exist as small particles in the wood. The delignification reaction takes place mainly within a three-dimensional region on the surface of the lignin particles. This results when the high sulfonation rate of the lignin causes the rate of diffusion of active chemical to the lignin to affect the sulfonation rate. The rate of delignification is hampered by this effect.

The effect of the reaction zone on the particle surface is combined with the effect caused by entrapment of reaction products within the lignin structure. This combination is called the physical accessibility phenomenon and is more detrimental to springwood delignification than to summerwood delignification. This results from the high spatial concentration of lignin in the springwood.

Reaction products which are in the process of diffusing through the cell wall at the time the reaction is stopped are not completely removed during washing of the pulp. This phenomenon has a retarding effect on the removal of lignin and is most pronounced for the summerwood.

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LITERATURE CITED

1. Hägglund, E., Svensk Kem. Tid. 44, no. 6:163-9(June, 1932).

2. Erdtman, H. Sulfite delignification of wood. In Wise and Jahn's Wood chemistry. 2nd ed. Vol. 2. p. 999-1020. New York, Reinhold Publishing Co., 1952.

3. Jahn, E. C. The lesser delignification processes. In Wise and Jahn's Wood chemistry. 2nd ed. Vol. 2. p. 1021-30. New York, Reinhold Publishing Co., 1952.

4. Stangeland, E., Papir-J. 20, no. 16:170-3(Sept. 21, 1932); no. 18:193-7 (Oct. 27, 1932); no. 20:214-17(Nov. 30, 1932); no. 24:272-4(Dec. 31, 1932).

5. Corey, A. J., and Maass, O., Can. J. Research 14B, no. 9:336-45(Sept., 1936).

6. Calhoun, J. M., Yorston, F. H., and Maass, O., Can. J. Research 17B, no. 4: 121-32(April, 1939).

7. Goldfinger, G., Paper Trade J. 112, no. 24:29-31(June 12, 1941).

8. Goldfinger, G., Paper Trade J. 113, no. 15:27-30(Oct. 9, 1941).

9. Brickman, W. J., Cabott, I. M., and Purves, C. B., Pulp Paper Mag. Can. 60, no. 2:T55-62(Feb., 1959).

10. English, H., Green, H., Mitchell, C. R., and Yorston, F. H., Forest Prod. Lab. Can. Pulp and Paper Lab. Quarterly Rev. no. 20:15-22(Oct.-Dec., 1934).

11. Haggroth, S., Lindgren, B. O., and Saeden, V., Svensk Papperstidn. 56, no. 17:660-9(Sept. 15, 1953).

12. Harlow, W. M. In Wise and Jahn's wood chemistry. 2nd ed. Vol. 1. p. 101. New York, Reinhold Publishing Co., 1952.

13. Bailey, A. J., Ind. Eng. Chem., Anal. Ed. 8, no. 1:52-4(Jan. 15, 1936).

14. Bailey, A. J., Ind. Eng. Chem., Anal. Ed. 8, no. 5:389-91(Sept. 15, 1936).

15. Bixler, A. L. M. The effect of digestion on wood structure. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1937. 167 p.

16. Bucher, H., and Widerkehr-Scherb, L. P. Morphology and structure of wood fibres. Attisholz/Solothurn (Switzerland), Research Laboratories of the Cellulosefabrik Attisholz AG, 1948. 31 p. 153 plates.

17. Lewis, H. F., and Richardson, C. A. II, Paper Trade J. 109, no. 14:48-50 (Oct. 5, 1939).

18. Jayme, G., and Köppen, Andreas von., Das Papier 4, no. 19/20:373-8; no. 21/22:415-20; no. 23/24:455-62(Oct.-Dec., 1950).

19. Lange, Paul W., Svensk Papperstidn. 50, no. 11B:130-4(June 15, 1947).

20. Kallmes, Otto, Tappi 43, no. 2:143-53(Feb., 1960).

21. Corey, A. J., and Maass, O., Forest Prod. Lab. Can. Pulp and Paper Lab. Quarterly Rev. no. 21:10-19(Jan.-March, 1935).

22. Nolan, W. J., Tappi 44, no. 11:753-62(Nov., 1961).

23. Nokihara, E., Tuttle, M. J., Felicetta, V. F., and McCarthy, J. L., J. Am. Chem. Soc. 79:4495(1957).

24. Goring, D. A. I., and Rezanowich, A., Can. J. Chem. 36, no. 12:1653-61(Dec., 1958).

25. Doraiswamy, K. The kinetics of pulping aspenwood with sodium sulfite solutions. Doctor's Dissertation. Madison, Wis., University of Wisconsin, 1952. 147 p.

26. Marth, Don. Studies on the lignin fraction of aspenwood pulps produced by sulfite-bisulfite cooking liquor systems. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1958. 143 p.

27. Brauns, Friedrich E. The chemistry of lignin. New York, N. Y., Academic Press Inc., 1952. 808 p.

28. Beazley, W. B., Johnston, H. W., and Maass, O. The penetration into wood of cooking liquors and other media. Ottawa, Dominion Forest Service Bulletin No. 95, 1939. 48 p.

29. Lange, P. W. The distribution of the chemical constituents throughout the cell wall. In Bolam's Fundamentals of papermaking fibres. Transactions of the symposium held at Cambridge, Sept., 1957. p. 147-85. Kenley, England, Technical Section of the British Paper and Board Makers' Association, Inc., 1958.

30. Kosilova, E. I., and Nepenin, N. N., Trudy Leningrad. Lesotekhn. Akad. no. 87:23-32(1959); Referat. Zhur., Khim. no. 19:489-90(1959); B.I.P.C. 30:927.

31. Glasstone, S., Laidler, K., and Eyring, H. The theory of rate processes. New York, McGraw-Hill Book Co., Inc., 1941. 611 p.

32. Busche, L. R., The klason lignin determination as applied to aspenwood with special reference to acid-soluble lignin. Doctor's Dissertation. Appleton, Wis., The Institute of Paper Chemistry, 1960. 109 p.

33. Vroom, K. E., Pulp Paper Mag. Can. 58, no. 3:228-31(Convention Issue, 1957).

APPENDIX I

ANALYSIS OF PULPS

LIGNIN ANALYSIS

The lignin content of the pulp was determined as the sum of the Klason lignin and soluble lignin. The details of this procedure are given below.

After a sample of pulp had been washed for three sequences in a tared extraction thimble immersed in distilled water it was given a wash with 95% ethyl alcohol to remove most of the water. The pulp was then extracted with a solution of 95% ethyl alcohol and benzene for four hours in a Soxhlet apparatus. The composition of this solution was 67% benzene and 33% alcohol by volume. After this, the pulp was washed with alcohol and extracted with 95% ethyl alcohol in the Soxhlet apparatus for an additional four hours.

The extracted pulp was removed from the extraction thimble and placed in a 100-ml. beaker. The extraction thimble was set aside to be used later for the determination of the amount of pulp which could not be transferred. The beaker of extracted pulp was placed in a vacuum oven overnight.

The extracted pulp was treated with 72% sulfuric acid for four hours with occasional stirring at a temperature which was held between 18 and 22°C. The mixture was then diluted to a 3% acid concentration and boiled for four hours in a beaker covered with a watch glass. Fresh distilled water was added to the boiling mixture when needed, to maintain the concentration at 3%.

After the acid treatment, the sample was filtered and washed with hot distilled water until the wash water became neutral to blue litmus paper. The

insoluble residue was dried and weighed as Klason lignin. The filtrate was collected, diluted, and analyzed for soluble lignin on the Beckman DU spectrophotometer.

For the summerwood pulps, 12 ml. of 72% sulfuric acid were used in the first step of the analysis and 450 ml. of distilled water were used for the dilution. The values for the springwood pulp were 10 ml. of sulfuric acid and 375 ml. of distilled water. The concentration of the sulfuric acid was measured to within $\pm$ 0.1% with a Westphal balance.

FILTERING TECHNIQUE

In preliminary experiments, it was found that the filtration of lignin was a very time-consuming process. The technique which is described below, however, was found to speed up the filtering process.

A pad of celite, approximately 1/16 inch thick, was placed in the bottom of a No. 4010 Selas crucible by means of filtration. The crucible was dried and its tare weight determined. During the filtration, when the filter became plugged, the acid was allowed to pass through the filter until the surface of the filter bed lost its luster. The surface of the celite cake was then carefully scraped with a small glass rod. This allowed the pores of the filter to become unplugged and filtration of the lignin could be continued. The glass rod was washed with a fine stream of distilled water from a wash bottle to avoid loss of the particles of lignin and celite which adhered to it.

SOLUBLE LIGNIN DETERMINATION

Busche (32) has shown that the analysis of soluble lignin can be carried out by spectrophotometric measurements at a wavelength of 208 mμ. From the

results of his work, Busche calculated an absorptivity of 105 ℓ./g.-cm. for the soluble lignin of aspenwood. This value was used to set up the calibration curve shown in Fig. 27. The linear portion of this curve has a slope equal to the absorptivity.

SULFUR ANALYSIS

EXPERIMENTAL

The sulfur content of the pulps was determined after six sequences of washing in distilled water.

The determination of sulfur was carried out by means of a Leco furnace. The instrument is a globar furnace with silicon carbide heating elements. Temperature of the furnace was maintained at approximately 2500°F. Passing through the furnace are two ceramic combustion tubes having an inside diameter of approximately 1 inch. The sample to be analyzed was placed in a small ceramic boat, covered with sand, and pushed into a combustion tube. Oxygen was passed over the sample and the gases bubbled through a Leco titrator. The sulfur is determined by an iodometric titration. A total time of approximately 15 minutes was required for each determination.

The sulfur content of the sample is given by the relationship

$$S = B\ F/2\ W$$

where S is the sulfur content in per cent, B is the buret reading, W is the sample size in grams, and F is a correction factor.

The correction factor can be determined from the relationship

$$F = G/5B$$

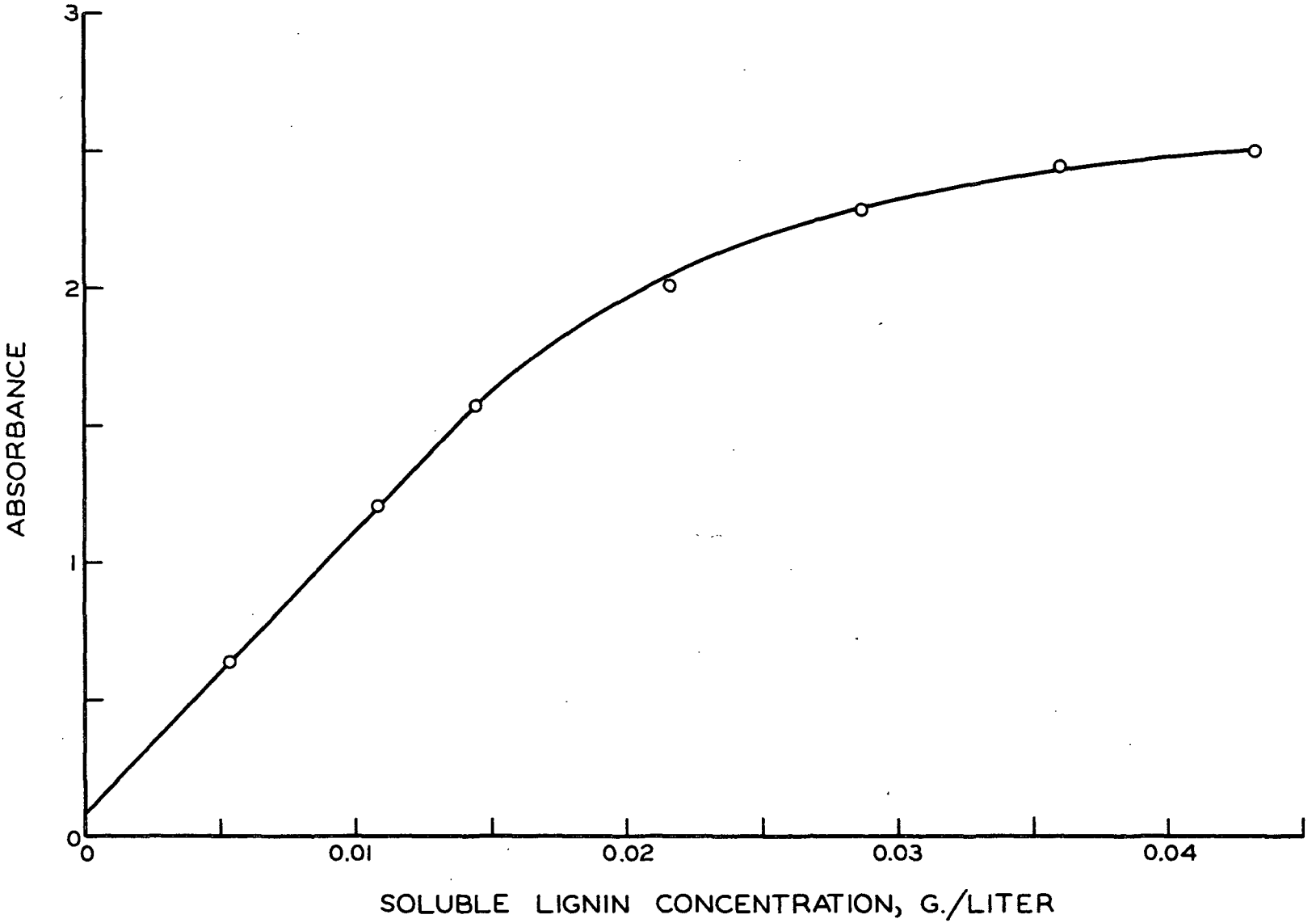

Figure 27. Spectrophotometer Calibration for Soluble Lignin Determination

where G is the weight of sulfur in milligrams which is used to calibrate the instrument. Sodium thiosulfate solution was found to be a good source of sulfur for the standardization. About 0.5 milligram of sulfur is sufficient for this purpose.

SAMPLE SIZE

A sample size of 0.05 gram of pulp was found to be best suited for the determination. If a sample size larger than about 0.07 gram is used, incomplete combustion results and unburned carbon comes through the apparatus as a fine powder.

CERAMIC BOATS AND SAND

Both the combustion boats and the sand which was used to cover the pulp sample absorb sulfur compounds from the atmosphere. It is necessary to "burn out" the boats and sand in the furnace before using them for sulfur determination. They can then be stored in a polyethylene bag or a tightly covered glass jar for at least one month before being used. Longer storage periods were not investigated.

ESSENTIAL DESIGN FACTORS

One of the products of combustion of wood pulp is water. If any water collects in the outlet tubes of the furnace, the analysis will be affected seriously by adsorption of sulfur dioxide in the water. Care must be taken to prevent this from happening. The following set of conditions must be observed.

1. The length of ceramic combustion tube which protrudes from the outlet side of the furnace must not exceed six inches from the outer wall of the furnace to the end of the constriction to prevent condensation inside the combustion tube.

2. Capillary tubing should be used to connect the combustion tube to the Leco titrator. Epoxy resin has been found to be an efficient cement for joining the glass tube to the ceramic combustion tube. One or two ground-glass ball joints should be placed in the line.
3. A washing system should be placed in the line to wash any condensed moisture into the titration chamber.

During an experimental run, moisture would condense inside the capillary tube near the combustion tube. After about five to seven minutes, the moisture had dried to about one-half the length of the capillary tubing. The remainder of the condensate was then washed into the titration chamber by means of a washing system.

APPENDIX II

CALCULATION OF AMOUNT OF EXCESS COOKING CHEMICAL ADDED TO THE WOOD BY PENETRATION

The excess cooking chemical in the porous structure of the wood can be calculated by means of a sulfur balance.

The maximum amount of sulfur required to dissolve the lignin in wood, S_r, is given by the relationship $S_r = S_L \; L \; W/1000$ where S_L is the maximum sulfur content of the residual lignin in per cent, L is the per cent lignin in the original wood, and W is the weight of the original wood. The value of S_L is calculated in the DISCUSSION and was found to be 4.3%. From the lignin content and weight of wood used in the cooks, S_r is found to be 0.009 gram for summerwood and 0.007 g. for springwood.

The amount of sulfur taken up by the wood during the penetration step S_p is given by $S_p = S_c \; C \; V/10{,}000$ where S_c is the per cent sulfur in sodium sulfite, C is the liquor concentration in g./ℓ., and V is the volume in milliliters of liquor which enters the wood during penetration. The liquor uptake of the springwood was found to be about 1.5 ml. and that of the summerwood was 0.3 ml. Since the liquor concentration was 105 g./ℓ., S_c is found to be 0.008 g. for summerwood and 0.04 g. for springwood.

The calculation shows that a large excess of chemical is introduced into the springwood during the penetration step. The summerwood, however, receives no excess cooking chemical but does contain almost enough chemical to complete the delignification reaction.

APPENDIX III

RELATIVE AMOUNTS OF CELL WALL LIGNIN IN SPRINGWOOD AND SUMMERWOOD

The lignin in a wood sample is equal to the sum of the cell wall lignin and the compound middle lamella lignin. This relationship is given by

$$L = 100L_m/M + W \tag{9}$$

where L is the lignin content in per cent, L_m is the mass of compound middle lamella lignin, M is the mass of the sample, and W is the cell wall lignin in per cent. From this equation, the amount of compound middle lamella lignin in a given volume of wood can be shown to be

$$L_m/V = (1 - W/L)\ M\ L/100V \tag{10}$$

where V is the volume of wood. By using the subscripts sp for springwood and sm for summerwood, Equation (10) can be written as two simultaneous equations.

$$(L_m/V)_{sp} = (1 - W_{sp}/L_{sp})\ M_{sp}\ L_{sp}/100\ V_{sp}, \tag{11}$$

and

$$(L_m/V)_{sm} = (1 - W_{sm}/L_{sm})\ M_{sm}\ L_{sm}/100\ V_{sm} \tag{12}$$

The amount of middle lamella lignin per unit volume was estimated from the fiber dimensions of springwood and summerwood as determined from a photomicrograph of loblolly pine. The thickness of the middle lamella was assumed to be the same for springwood and summerwood. The ratio of springwood middle lamella to summerwood middle lamella was found to be about 0.8 for similar wood volumes. Therefore,

$$(L_m/V)_{sp} = 0.8\ (L_m/V)_{sm} \tag{13}$$

Solution of Equations (11), (12), and (13) shows the fraction of the total lignin which is contained in the summerwood cell wall to be

$$(0.8)(W_{sm}/L_{sm}) = 1 + (W_{sp}/L_{sp} - 1)(M_{sp}\ L_{sp}\ V_{sm}/M_{sm}\ L_{sm}\ V_{sp}) \quad (14)$$

Equation (14) can be solved by considering equal volumes of springwood and summerwood. Table I shows the average volumes of two summerwood slivers and one springwood sliver to be equal. The value of $M_{sp}\ V_{sm}/M_{sm}\ V_{sp}$ can be found by calculation of the ratio of the average mass of one springwood sliver to the average mass of two summerwood slivers. The average mass of a springwood sliver was found to be 0.04152 gram and the average mass of two summerwood slivers was 0.13160 gram. The number of slivers which were used for the calculation was 1248 springwood slivers and 1128 summerwood slivers. The value of $M_{sp}\ V_{sm}/M_{sm}\ V_{sp}$ therefore is 0.316. Using this value and the lignin contents of 28.5% for springwood and 25.9% for summerwood, Equation (14) becomes

$$W_{sm}/L_{sm} = 0.565 + 0.435\ W_{sp}/L_{sp} \quad (15)$$

Equation (15) shows that the fraction of summerwood lignin contained in the cell wall must be greater than the fraction of springwood lignin in the cell wall. The value of W_{sp}/L_{sp} is unknown but is probably small because of the very thin walls of the springwood fibers. The value of W_{sm}/L_{sm} however, cannot be less than 0.565 or about one-half of the summerwood lignin. Clearly then, if one assumes that most of the springwood lignin is contained in the compound middle lamella, the summerwood must contain most of its lignin in the secondary wall.

APPENDIX IV

CALCULATION OF COOKING TIME CORRECTION

The heating up of the digesters has been shown to take place within 90 seconds after they are placed in the hot oil bath. Any correction in the cooking time which must be made to account for this heating up period will be small in magnitude. This correction is necessary however, if initial rates are to be calculated from the data at 175°C. because of the short reaction time which is required to obtain data in the high-yield range. Conversely, the correction is insignificant at 138.5°C. because of the long pulping times.

In the collection of experimental data, reaction time was measured from the time a digester was placed in the oil bath until the time that it was placed into ice water. To correct the cooking time, therefore, the time correction must be subtracted from the measured time. The time correction in seconds will be given by

$$\theta = 90 - I \qquad (16)$$

where θ is the time correction and $\underline{I}$ is the cooking time which would be required at the cooking temperature to remove the amount of lignin which is dissolved during the 90-second heating up period. $\underline{I}$ can be called the equivalent cooking time of the heating up period.

If the rate of delignification during the heating up period is

$$dL/dt = - K f(L) \qquad (17)$$

then,

$$\int_{L_o}^{L} dL/f(L) = -\int_{o}^{t} K \, dt \qquad (18)$$

where L is the amount of lignin present at time t, L_o is the initial lignin, f(L) is an unknown function of L, and K is the rate constant and is related to the temperature. Under constant temperature conditions, K is constant and

$$\int_{L_o}^{L} dL/f(L) = -K_m \int_{o}^{t_m} dt_m \qquad (19)$$

where the subscript m refers to the conditions at maximum temperature. For the same amount of lignin removal at maximum temperature as takes place during the heating up period, Equations (18) and (19) can be combined to give

$$\int_{o}^{t_m} dt_m = I = \int_{o}^{t} (K/K_m)dt \qquad (20)$$

The values for the rate constants in Equation (20) are given by the Arrhenius relationship

$$K = A \exp(-E/R\ T) \qquad (21)$$

and

$$K_m = A \exp(-E/R\ T_m) \qquad (22)$$

where T is the absolute temperature, E is the activation energy, and R is the ideal gas constant. By substitution,

$$I = \int_{o}^{t} [\exp(E/R)(T - T_m)/T\ T_m]\ dt \qquad (23)$$

The value of I is found by graphical integration of Equation (23). In order to do so, however, the relationship between temperature and time must be known. The measured temperatures cannot be used because lag in the thermocouple and recording instrument cause these values to be too low. The relationship between temperature and time, therefore, will be assumed to be a simple exponential approach to equilibrium, or

$$T = T_m - (T_m - T_o) \exp - t/Q \qquad (24)$$

where Q is the time constant of the system, and T_o is the initial temperature. The time constant has been estimated from the experimental measurement of temperature to be about 14 seconds.

The values used in the graphical integration are given in Table IX. For convenience, the term in brackets in Equation (20) will be called X. That is,

$$X = \exp (E/R)(T - T_m)/T\,T_m \qquad (25)$$

TABLE IX

VALUES USED IN GRAPHICAL INTEGRATION

Initial Temperature = 30°C.
Final Temperature = 175°C.
Activation Energy = 22,000 cal./g.-mole

Time, seconds	Temperature,[a] °K.	X
0	303.0	0.000+
14	394.5	0.035
28	431.3	0.382
62	441.9	0.710
56	445.8	0.885
70	447.2	0.957
84	447.7	0.984
90	448.0	1.000

[a]Calculated from Equation (24).

The values of Table IX are shown in Fig. 28. Integration of the curve gives an equivalent time of 55 seconds. From Equation (16), therefore, the time correction is 35 seconds.

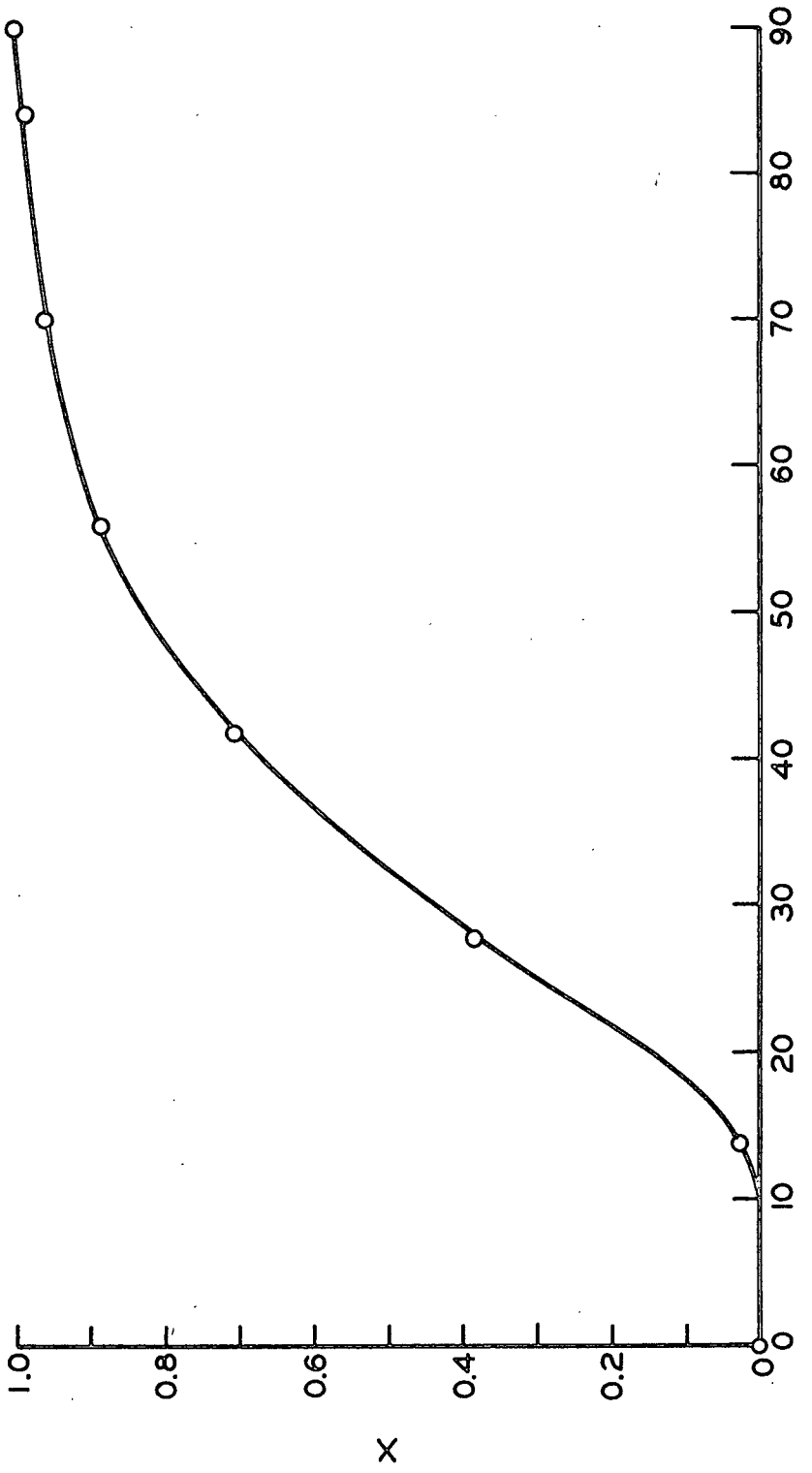

Figure 28. Values of X vs. Time for Graphical Integration of Equation (23)

The correction necessary for the cooling of the digesters has been found to be insignificant.

A similar method for the calculation of equivalent time is given by Vroom (33) who used an integrated relationship for lignin as a function of time as the basis for his derivation.

APPENDIX V

DERIVATION OF RATE EQUATIONS FOR HYDROLYSIS OF AN IDEAL POLYMER

It is of interest to show how molecular weight influences the rate at which a polymer is dissolved when the dissolution mechanism requires a degradation of the polymer. A monodisperse, linear polymer will be assumed in which all possible sites for hydrolysis have an equal probability of being cleaved by the reaction. Further, it will be assumed that secondary valence forces limit the maximum molecular weight of soluble polymer.

If s is the total number of reaction sites per gram of polymer, the rate of hydrolysis per gram will be

$$ds/dt = - k s \qquad (26)$$

where t is time and k is the hydrolysis rate constant. Integration of this equation gives

$$s = s_o \exp (-k t) \qquad (27)$$

where s_o is the number of reaction sites originally present in the polymer. If C is defined as the most probable number of chain cleavages necessary to completely dissolve a gram of polymer, the fraction of polymer which has been dissolved will be

$$(P_o - P)/P_o = (s_o - s)/C \qquad (28)$$

where P is the amount of undissolved polymer, and P_o is the amount of polymer originally present. Combining Equations (27) and (28) gives

$$P = P_o - (P_o s_o/C) + (P_o s_o/C) \exp (-k t) \qquad (29)$$

Differentiating Equation (29) and combining with Equations (27) and (28) gives

$$dP/dt = -k\,P + k\,P_o - k\,P_o s_o/C \qquad (30)$$

where the values of s_o and C are dependent upon the molecular weight of the polymer. Evaluation of the relationship between s_o/C and molecular weight, therefore, will show how the rate of dissolution is influenced by molecular weight.

If B is the molecular weight of one monomer, and a is the number of monomers in the largest soluble molecule, then the molecular weight M, of a polymer molecule will be

$$M = n\,a\,B \qquad (31)$$

where n is the smallest number of soluble fragments into which the polymer molecule can be divided. The number of sites per gram is

$$s_o = (N/m)\,(n\,a - 1) \qquad (32)$$

where (N/m) is the number of polymer molecules per gram and is equal to Avogadro's number divided by the molecular weight. Thus,

$$s_o = (N_o/n\,a\,B)\,(n\,a - 1) \qquad (33)$$

where N_o is Avogadro's number.

Consider N molecules of polymer each of which has a molecular weight of M. After degradation of the polymer there will be N_f molecules of degradation products. The total number of chain cleavages, H, will be given by

$$H = N_f - N \qquad (34)$$

The number of polymer molecules is related to the total mass of polymer m by the expression

$$N_p = m\, N_o/M \tag{35}$$

where N_o is Avogadro's number. Combining Equations (34) and (35) gives

$$C = H/m = N_f/m - N_o/M \tag{36}$$

where C is the number of cleavages per gram of polymer. The number of degradation product molecules is

$$N_f = \sum N_i \tag{37}$$

where N_i is the number of product molecules having a molecular weight of M_i. In addition, the mass is given by

$$m = \sum N_i M_i / N_o \tag{38}$$

Dividing Equation (37) by Equation (38) gives

$$N_f/m = N_o \sum N_i / \sum N_i M_i = N_o/M_n \tag{39}$$

where M_n is the number average molecular weight of degradation products. Combining Equations (36) and (39) gives

$$C = N_o\, [(1/M_n) - (1/M)] \tag{40}$$

In order to find the number of cleavages necessary to completely dissolve the polymer, any degradation which takes place on a polymer fragment after it has been dissolved must not be considered. In order to define M_n, therefore, the molecular weight of a reaction product must be treated as if it remains constant after it has been sufficiently degraded to become soluble.

If the degradation is considered to be random, it is clear that the soluble products will have a distribution of molecular weights. The molecular weights of the products can be expected to consist of integral units of B ranging from a value of B to a value of a B. In a random degradation, the probability that a soluble product will have any one of these molecular weights is the same as the probability that it will have any other of these molecular weights. Therefore, after a random degradation which is completed only at the point at which soluble fragments remain which are not further degraded, the number of product molecules at each level of molecular weight will be equal. From the definition of number average molecular weight, it follows that

$$M_n = (a\ B + B)/2 \qquad (41)$$

Equations (40), (41), and (31) can be combined to give

$$C = N_o/B\ [2/(a + 1) - 1/a\ n] \qquad (42)$$

Dividing Equation (33) by Equation (42) gives

$$s_o/C = (n\ a - 1)\ (a + 1)/(2\ n\ a - a - 1) \qquad (43)$$

Equation (43) can be combined with Equation (30) to show the effect of the molecular weight of the polymer on its rate of dissolution.